Translated from *Uspekhi Khimii*, 47, 1756 - 1773 (1978) U.D.C. 541.49

Coordination Chemistry in Italy: The Work of the Rome School

C.Furlani

The principal directions of the development of coordination chemistry in Italy (the Rome school) are considered in their historical aspect. In the field of the theory of the structure of complex compounds research on the ligand field theory and calculations by the molecular orbital methods are being carried out in Rome. Numerous studies on the synthesis and determination of the structures of many new complexes are examined and the kinetics and mechanisms of chemical reactions of coordination compounds, mainly substitution reactions, are discussed. Much attention is devoted to the investigation of the properties of complexes with the aid of various physical methods—electronic and photoelectron spectroscopy, vibrational spectroscopy, magnetic resonance methods (EPR, NMR, NQR), and electrochemical methods (particular polarography). Studies related to the preparation of catalytically active complexes and their properties are also considered.
The bibliography includes 247 references.

CONTENTS

I.	Introduction	944
II.	Principal fields of research	944
III.	Theory of coordination binding	945
IV.	Syntheses	945
V.	Kinetics and mechanisms of reactions	947
VI.	Electronic spectroscopy	948
VII.	Vibrational spectroscopy	948
VIII.	Electrochemistry	948
IX.	Other methods	949
X.	Applied research	950

I. INTRODUCTION

Coordination chemistry has been very popular in Italy for a very long time. During the period when Werner developed intensive investigations in Zurich, Miolati in Padua studied the structure of polyacids. In the next decade Cambi, Natta, and other well known chemists carried out the first studies in the field of metal complexes. Soon after the second world war Italian scientists participated in the development of all the fields of modern coordination chemistry, so that at the present time studies on the coordination compounds are prosecuted in almost every Italian university. Several particularly active scientific centres arose, the most important of which are those in Milan, Padua, Florence, and Rome. The present review gives a brief historical description of the development of the Rome centre and also the results of scientific research carried out in the last few years and being prosecuted at the present time.

The work of Professor Vincenzo Caglioti, who laid the foundations of the Rome school during the war and in the subsequent years, has had the greatest influence on the development of coordination chemistry in Rome. These studies are now being continued by Prof.Guido Sartori and many of his coworkers, working both in the Rome University and in other Italian institutes. This review will therefore survey the results of research by the chemists in the Rome school working in more or less closely related fields at the following institutes: the Institute of General and Inorganic Chemistry at the Rome University; the Laboratory of the Theory of the Electronic Structures and Spectrochemical Properties of Coordination Compounds of the National Research Council of Italy in Rome; the Institute of General and Inorganic Chemistry at the Peruggia University. In addition, mention will be made of some of the studies carried out at the Chemical Institute of the University of Trieste.

II. PRINCIPAL FIELDS OF RESEARCH

Traditionally the work of the Rome school on coordination chemistry, which began in the 1930's with early polarographic studies[1-4], embraced a wide range of fields, including almost all the aspects of the chemistry of metal compounds—from the fundamental theory to problems of industrial applications. However, studies on the electronic structures, stereochemistry, spectroscopy, and related problems have developed to the greatest extent; thermodynamics and resonance spectroscopy have been less well developed. The consideration of various aspects of this research may be divided into eight sections:

(1) theory of the coordinate bond;
(2) syntheses of new coordination compounds and determination of their structures by X-ray diffraction analyses;
(3) kinetics of substitution reactions involving metal complexes;
(4) electronic spectroscopy;
(5) vibrational spectroscopy;
(6) electrochemistry;
(7) various research methods;
(8) applied research.

This subdivision is undoubtedly extremely arbitrary, some of the relevant studies being carried out simultaneously. For example, syntheses have been frequently performed in order to obtain complexes which might confirm theoretical principles; electrochemical studies in non-aqueous solvents made it possible to characterise and synthesise complexes unstable in an aqueous medium; X-ray diffraction studies went hand-in-hand with the spectroscopy of single crystals, etc.

III. THEORY OF COORDINATION BINDING

The interest of the Rome school in research on the nature of bonds in complexes arose in the 1950's when Hartmann's work[5] demonstrated the entire importance for chemistry of the crystal field model developed by Bethe[6], Van Vleck[7], and others and laid the foundations of the modern ideas about the coordinate bond. Early contacts of Italian chemists with Hartmann's group[8-10] ensured that the ligand field theory became widely known in Italy. This led to the appearance in 1957–1964 of a large number of publications devoted to the interpretation (from the standpoint of this theory) of the structures and spectra of complexes having a definite electronic configuration, particularly the d^6 configuration in high-spin complexes of iron(II)[11,12] and the d^8 configuration in systems with high-spin and low-spin states, for example, in Lifshitz salts[13,14], metal dicyclopentadienides[15], and many tetrahedral halogeno-complexes of Series I transition metals. The development of theoretical postulates was followed by the syntheses of new complexes[16-20]. Since then the ligand field theory has been constantly used for a preliminary interpretation of the results of synthetic and spectroscopic studies by the Rome school. Furthermore, two other fields of theoretical research are being developed: the improvement of the models of the ligand field theory and attempts at a complete description of coordination compounds with the aid of the molecular orbital method.

Among the early studies, an interesting investigation was carried out—namely a detailed analysis of the magnetic susceptibility of d^2 systems[21]. This investigation was followed by an extensive review of the applications of the ligand field theory to the interpretation of the structures and spectra of complexes with a coordination number of five, published in 1968.[22] Subsequently a series of coordination compounds were synthesised and the spectra and structures of their single crystals were investigated: (see below). Numerous studies were performed on the electronic spectra of single crystals, in which the potential possibilities of the ligand field theory for the interpretation of the spectra were used more fully. They will be examined in detail in the section devoted to electronic spectroscopy. The angular overlap method, devised as a development and a revised version of the ligand field theory, was used in certain cases. This model proved to be suitable for the description of the ligand field spectra of the square-pyramidal complex $Fedtc_2Cl_2$[23] and certain high-spin adducts of the square planar nickel(II) complex $Nidtp_2py_2$.[24] (Here and henceforth dtc = dithiocarbamate, dtp = dithiophosphate, and py = pyridine.)

Calculations on coordination compounds by the molecular orbital method were proposed at the beginning of the 1960'S as an alternative to the ligand field model (the limitations of which are now more clearly seen; its advantages for approximate estimates have also been established). A large number of more or less complex new versions of the molecular orbital method immediately arose and, although none of them can be used as yet without difficulty, they have been extremely valuable.

Theoretical studies of this kind aroused the interest of the Rome school. The problem of such studies was formulated in 1967 at the Symposium on Theoretical Inorganic Chemistry organised by the Peruggia group[25]. After that, certain models for semiempirical calculations by the molecular orbital method, for example, the "full overlap"[26], "zero differential overlap", and analogous methods[27], were developed at the Rome school and tested in practice. Particular attention in the course of this research was devoted to allowance for the effect of open shells (using the Roothaan operator technique).

Despite this, certain calculations on model molecules, such as $[TiF_6^{3-}]$, showed that semiempirical methods of this kind suffer from serious disadvantages. They are associated with difficulties in the parametrisation of empirical quantities. One can now assume that the most promising are the onn-empirical (*ab initio*) computational methods as well as simple semiempirical methods, which, although fairly approximate, are simple to use. As an example, one may quote the improvement of the Wolfsberg–Helmholtz model based on the extensive employment of the Mulliken approximation for the estimation of the contribution of each molecular integral. This model has been used successfully for a number of sulphur-containing complexes, for example $Nidtp_2$ and $Nidtc_2$.[28] As regards the intensification of attempts at the improvement of this method, one may also consider the procedure developed by Fencke where, instead of simple adjustment for self-consistency or the self-consistency of atomic charges, the requirement of the Hartree–Fock SCF is introduced and (or) one uses as a basis for molecular orbital calculations the atomic orbitals obtained by adjustment for self-consistency under the condition of perturbation of the ligand field in the complex investigated, and not the atomic orbitals of free atoms or ions[29].

IV. SYNTHESES

This section deals with the studies in the last decade which have been devoted mainly to complexes containing chalcogenide ligands. The interest in these complexes, where sulphur or selenium serve as donors, arose because of the wide variety of the electronic structures and stereochemical rearrangements and the possibility of comparing them with donor ligands containing oxygen. Thus in the case of sulphur we have a complete set of ligands: a weak field ligand and at the same time a strong π donor S^{2-}, chelating anions of the type dtc^- (R_2NCS_2), dtp^- (R_2PS_2), or dithiocarboxylates ($R-CS_2^-$) (the π-donor and spectrochemical properties of which are extremely different and depend to a large extent on the nature of R), simple neutral thioesters (R_2S), conjugated neutral ligands such as thiourea ($R'R''N-CS-NR'''R''''$) or thiocarbamate esters ($R'OCS-NR''R'''$), and, finally highly conjugated dithiolates.

A spectrochemical comparison of S^{2-}, Se^{2-}, and Te^{2-} by examining the spectra of tetrahedrally coordinated cobalt(II), introduced into the lattices of compounds of the type ZnY or CdY (Y = S, Se, or Te), proved possible for the first group of chalcogenide ligands[30]. The principal studies on chelating dithio-anions were carried out for dithiophosphate complexes. In particular, studies were made on the spectra of nickel(II) dithiophosphates (R = C_6H_5 or C_2H_5O) and their high-spin pseudo-octahedral adducts with nitrogen-containing bases and their X-ray diffraction analysis was carried out[31-34].

The addition of primary aliphatic amines to $Nidtp_2$ takes place in two stages via the formation of a five-coordinated high-spin intermediate, the spectra and reversible formation reactions of which have been studied in detail[35,36]. Other five-coordinated $Nidtp_2$ adducts have been studied by the method of the polarised spectra of single crystals[37]. The same method has been used to compare the properties of a number of phosphorus(III) compounds—dithiophosphates ($Mdtp_3$ or $Mept_3$) dissolved in $Indtp_3$ matrices containing the corresponding dithiocarbamates (In, M)dtc_3.[38] The vanadium(III) compound $Vdtp_3$, synthesised for the

first time, is of special interest [39,40]. The reactions of dithiophosphate complexes with bidentate phosphorus and arsenic bases have been investigated [41,43]. As regards dithiocarbamates and related compounds, apart from a few early data on their X-ray diffraction analysis [43-45], systematic studies have been made on the analogous diselenocarbamates $Mdsec_2$, where dsec = $(C_2H_5)_2NCSe_2^-$. These compounds are largely similar to dithiocarbamates, but, in estimating their spectrochemical parameters, it is possible to make interesting quantitative comparisons of their properties.

In parallel with the syntheses and spectroscopic studies [46,47], X-ray diffraction studies have also been made on copper(II), [48] nickel(II), [48,49] and zinc(II) [48] complexes. An analogous comparative study of sulphur and selenium compounds has been made for xanthates: several new metal diselenoxanthates $(ROCSe_2)_nM$ were synthesised and studied spectroscopically [50], but they proved to be less stable and less suitable for investigation than diselenocarbamates and diselenophosphates.

From the standpoint of their structures, the dithiocarbazinates ($R_1R_2N-NR_3-CS_2^-$ = dtcz) resemble dithiocarbamates, but they exhibit a greater variety of coordination stereochemistry, since they can behave as bidentate S,S- or S,N-ligands. This depends on several factors, such as the nature of the metal ion, the nature of the substituents influencing the basicity of the nitrogen atoms, and steric conditions. For example, the compounds $Nidtcz_2$ are low-spin square complexes usually forming N,S-chelates in the presence of aliphatic substituents or without substituents and S,S-chelates in the presence of aromatic substituents [51,52]. The complexes of bivalent palladium and copper exhibit similar properties, while zinc shows a greater tendency to form pseudotetrahedral S,S-chelates [53]. The pseudo-octahedral chromium(III) and cobalt(III) complexes can form either S,S- or S,N-chelates [54].

Nickel(II) complexes have been most thoroughly investigated: X-ray diffraction [55,56] and NMR studies [57,58] made it possible to elucidate their coordination stereochemistry and the conformations of the added ligands. These complexes are exceptionally reactive. They undergo deprotonation [59] and alkylation [60] very readily, form labile adducts with oxygen [61], and undergo an unusual cleavage of the N-N bond with formation of the corresponding dithiocarbamates [62].

The dithiocarbazinate esters $R_1R_2N-NR_3-CSSCH_3$ are also effective ligands, forming in the deprotonated form square inner complexes and 1 : 3 pseudo-octahedral complexes with nickel(II). [63] A number of organic reactions of these esters have been studied [63]. Systematic investigations of the corresponding thiocarbazates $R_1R_2N-NR_3-COS^-$ are being prosecuted at the present time [64] and their results will make possible numerous comparison with other compounds, including the hydrazinecarboxylate complexes $(H_2N-NH-COO)_nM$ already known in the literature [65-67].

Studies on the complexes of simple dithiocarboxylic acids R-CSSH or LH (R = alkyl or aryl) are being most vigorously prosecuted; such acids give rise to the simplest possible dithio-anions, but until 1968 they were scarcely used as ligands. Systematic studies, begun in Peruggia, showed that these ligands behave fairly strangely. Thus, although they form inner complexes with the usual stereochemistry (pseudo-octahedral $M^{III}L_3$, square $M^{II}L_2$), a greater degree of mixing of the ligand and metal orbitals (possibly associated with the low electronegativity of R compared with that of R_2N^-, RO^-, etc. in other dithio-anions) is more characteristic of their electronic structure. This is clearly seen, for example, in the electronic spectra, which frequently differ from the usual spectra corresponding to models of the ligand field theory [68]. It has been observed that low-spin nickel(II) complexes [68,69] are not monomeric but form weakly bound trimers Ni_3dtb_6†, [70,71] bridged dimers of the type Ni_2dtpa_4, [31,72] or axial dimers Ni_2dtpv_4, [69,73] or even more complex trinuclear structures of the kind found for dithioacetate [74]. Structures of the type of bridged dimers have also been observed for complexes of monothiobenzoates Ni_2mtb_4. .EtOH (pseudo-octahedral coordination of metal atoms) [75] and Co_2mtb (tetrahedral coordination of the metal) [76], while chromium gives rise to the monomer $Crmtb_3$. [77] Complexes of dithiocarboxylates are also remarkable due to the fact that they are readily transformed into complexes of perthiocarboxylates $R-C(=S)-S\cdots M/n$, which are also being vigorously investigated by spectroscopic [78] and X-ray diffraction [79] methods. Complexes of thiourea with *N*,*N*′-substituted ligands RHN-CS-NHR′, in the case where they exist with the most preferred stereochemistry [for example octahedral stereochemistry for chromium(III) [80] or pseudotetrahedral stereochemistry for cobalt(II) and zinc [81-83]], and when there exist numerous coordination forms, possibly depending on the nature of the substituents R and R′, have been investigated in particular detail. Thus thiourea forms 1 : 4 complexes with palladium(II) and platinum(II), which do not have a simple square structure but are five-coordinated compounds $[ML_4X]^+$ (M = Pd or Pt, L = substituted thioureas, X = halogen or ClO_4) by virtue of the π-acceptor properties of the ligands [84]. On the other hand, in the presence of a molar deficiency of L or an excess of X^-, the complexes ML_2X_2 are formed [84-86]; their formation is also possible in the case of a complex equilibrium.

N,*N*′-Disubstituted selenoureas RHN-CSe-NHR′ behave in relation to palladium(II) and platinum(II) like their sulphur-containing analogues, giving rise to complexes with the same structures and stabilities, let alone the shifts in the spectra [84,87].

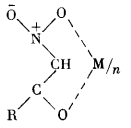
Thiocarbamate esters have also been studied, although they exhibit an extremely weak affinity for d^8 metal ions. Their coordination number does not usually exceed two and they are bound, whenever possible, not to the C=S group but to other electron-donating groups, for example the allyl group in PdL_aCl_2 ($L_a = CH_2=CH-CH_2-NH-CS-OCH_3$) or the deprotonated nitrogen atom in PdL''_2 ($L'' = C_5H_5N^- - CS-OCH_3$). [88-90]

Although the complex-forming properties of thiourea in relation to nickel(II) had been known earlier, they were studied in detail by the present author. Nickel(II) complexes of *N*,*N*′-substituted thio- and seleno-ureas were investigated, which yielded evidence for the existence of different coordination forms and stability series. These series include [91-93] the octahedral chromophores $[NiS_6]$ in certain compounds of the NiL_6X_2 (X = Cl, Br, or I) series and in certain crystalline solid $NiL_6(ClO_4)_2$ specimens, tetragonal chromophores $[NiS_4...X_2]$ in solid NiL_4X_2 specimens, which are in certain cases characterised by a singlet-triplet equilibrium in the ground state, pseudotetrahedral $[NiL_2X_2]$ groups, which exist in the solid form only for fairly bulky ligands but are protonated much more readily in solution, and square $[NiS_4]$ groups, for example,

† Here and henceforth dtb = dithiobenzoate and dtpa = dithiophenylacetate.

in thiourea perchlorates (they also formed very readily with selenoureas[94]). Later we began to study complexes of polydentate ureas such as $H_2N-(CH_2)n-NH-CS-NHR$ and $RHN-CS-NH-(CH_2)n-NH-CS-NHR$.[95,96]

Yet another class of ligands, which has been studied in detail in the Rome laboratory, are the α-nitro-ketones $R-CO-CH_2-NO_2$ (mainly $C_6H_5-CO-CH_2-NO_2$) which give rise to chelate rings



analogous to the chelates formed by β-diketones. The greatest number of studies have been devoted to the copper complexes CuL_2 and their five- and six-coordinated adducts[97-100], for which interesting instances of conformational isomerism may be observed. Nickel(II), cobalt(II), and other transition metal complexes have also been investigated[101-104]. Unusual ligand cleavage reactions have been discovered for platinum and gold nitroketonates[105]. The properties of organic nitro-compounds as ligands are always of interest and studies on *gem*-dinitro-compounds $RCH(NO_2)_2$ have been carried out in this connection[106].

The behaviour of hydrazine as a ligand is also of interest, because this compound is a bidentate donor but does not exhibit a capacity for chelate formation. This is evident from the analysis of the spectra and structures of certain nickel(II) complexes with hydrazine and mixed ligands[107-109]. Further synthetic, structural, and spectroscopic investigations dealt with rhenium[110], titanium(II),[111] silver(II),[112] niobium(V),[113] molybdenum(III), and molybdenum(V)[114,115] complexes and transition metal complexes of phthalocyanines (known to exhibit a quasi-reversible NO absorption)[116-118].

In this section we shall also mention studies devoted to complexes of quaternary diphosphine bases and related ligands[119-121] as well as studies on equilibria in solution. Although these investigations have not been part of the main field of research of the Rome school and have not been carried out systematically, they were performed to explain the properties of the less stable compounds. Apart from the early investigations of the copper(II) complexes of aliphatic diamines with long chains[122], 1:1 and 1:2 paramagnetic adducts of the square $[NiS_4]$ complexes of amines, for example, $Nidtp_2$, have also been studied[26,35]. The stability constants of zinc(II) and cadmium tartrates and citrates in water[123], of cobalt(II) complexes of halogenophosphines in organic solvents[124,125], and of mercury(II) halides in acetonitrile[126] were investigated.

V. KINETICS AND MECHANISMS OF REACTIONS

The study of the reactivities of coordination compounds has been of continued interest at the Chemical Institute of Rome University. Attempts were made to elucidate the mechanisms of substitution in octahedral cobalt(II), rhodium(III), and iridium(III) amino-complexes. Most attention has been devoted to the behaviour of monodentate ligands–carboxylates–in hydration reactions and (or) alkaline hydrolysis in order to establish analogies between these compounds and organic esters[127-133]. Whenever possible, the kinetic data were analysed by plotting linear free energy relations in order to estimate the influence of the geometrical and electronic structures on the kinetics. In order to discover whether the metal–oxygen or the carbon–oxygen bond is ruptured, experiments using ^{18}O were performed in the most interesting cases. It was found that in neutral or alkaline media hydration proceeds mainly via a dissociative mechanism with rupture of the metal–oxygen bond (acid catalysis takes place at low pH values). The alkaline hydrolysis proceeds either via an S_N1CB mechanism, which is typical of octahedral amino-complexes, or via a B_AC2 mechanism which is typical of organic esters. In addition, a third reaction pathway, which gives a second order dependence on OH^- and involves the dissociation of the carbon–oxygen bond, was discovered. This mechanism has no analogies in the hydrolysis of esters.

Water exchange reactions were investigated for $[Rh(NH_3)_5(H_2O)]^{3+}$ and $[Ir(NH_3)_5(H_2O)]^{3+}$ and a comparison was made with anation reactions in order to elucidate the role of the interacting groups[134-137]. It was found that, in contrast to the analogous cobalt(III) compounds, the reactions of heavier d^6 metals have an appreciably associative mechanism. This conclusion, supported by modern studies designed to determine the activation volumes in the exchange involving water[138], was unexpected, because numerous kinetic data accumulated for cobalt(III) complexes led to the conclusion that the main reaction pathway for all octahedral complexes involves a dissociative mechanism.

A study was made of the role of the leaving groups in substitution reactions involving certain monoacidic octahedral cobalt(III) and chromium(III) complexes. A linear relation was discovered between the free energies derived from the aquation constants and the values of K_a for the conjugate acids forming part of the ligand[139]. Reactions of the nitrate ion are anomalously rapid from this standpoint, although experiments with ^{18}O showed that its substitution by water proceeds via the dissociation of the metal–oxygen bond[140]. The properties of the nitrate ion as the leaving group have been the subject of special studies[141]. In the series of compounds nitratopentaminecobalt(III), nitratopentaminerhodium(III), and nitratopentamineiridium(III), the NO_3^- anion undergoes alkaline hydrolysis via the usual coupling mechanism, possibly with nucleophilic insertion of a water molecule in the case of heavier metals (S_N2CB). The entropy data show that the freedom of rotation, of which the anion is capable in the transition state, tends to diminish in the sequence $Co > Rh > Ir$.

The series of studies on the reaction mechanisms includes also research into substitution in uncharged ruthenium(II) complexes in non-aqueous solvents[142,143]; kinetic data indicate the formation of five-coordinated intermediates. A study was also made of the hydrolysis and *cis–trans* isomerisation in anionic aquo-complexes of ruthenium(IV), containing bidentate ligands (carboxylates)[144]. It appears that the isomerisation mechanism in these instances changes from dissociation at one end of the molecule to dissociation in water with increase of the number of atoms in the chelate ring.

Investigation of the properties of metallocenes in order to elucidate the nature and the site of the interaction of protonating agents with these molecules constitutes a relatively new field[145,146]. The important role of the cyclopentadienyl ring as the basic centre of the molecule was observed[147]. Further studies were devoted to the hydrogen–deuterium exchange in various protic media[148]. The stability constants of certain ferrocenyl carbonium ions were determined and were used to estimate the electron-donating properties of ferrocenyls.

VI. ELECTRONIC SPECTROSCOPY

The study of the electronic absorption spectra of complexes is associated both with theoretical investigations (mainly the assignment of bands in the visible region from the standpoint of the ligand field theory) and with investigations in the field of syntheses, and is part of almost all the publications mentioned in previous sections. Studies devoted to the interpretation of the electronic spectra of coordination compounds, obtained for specimens in the form of single crystals using polarised light, are of special interest for spectroscopy. This field is being developed by the Rome laboratory simultaneously with crystallographic X-ray diffraction investigations. These research techniques make it possible to employ at a deeper level the interpretative possibilities of the ligand field theory with the aid of rigorous selection rules and are widely used in the modern research by the Rome school. The following systems have been investigated: $[CuCl_4]^{2-}$ chromophores with pseudotetrahedral [149] and square planar [150] structures; square $[NiS_4]$ chromophores [151]; certain types of trigonal octahedral complexes of tervalent transition metals with bidentate sulphur-containing ligands [38-40]; the dinuclear complex $Nidtpa_4$ (where dtpa = dithiophenylacetate) [72]; pseudotetrahedral cobalt(II) complexes with various *s* and *p* donors [152]; the $[MnCl_5]^{2-}$ ion [153]; eight-coordinated tetranitrato-complexes [154]; and certain other transition metal complexes, mainly those of nickel and copper.

Another spectroscopic method, which has been developed particularly vigorously in recent years in Rome and Peruggia, involves the study of the luminescence spectra of inorganic chromophores. Both fluorescence and phosphorescence spectra yield important information for the determination of the positions and the identification of excited electronic levels and thus supplement data obtained with the aid of absorption data. Furthermore, luminescence spectra make it possible to study phenomena involving excitation via structural energy transfer and the reactivities of metal complexes. Despite its considerable advantages, emission spectroscopy is used much more rarely than absorption spectroscopy, possibly because of considerable technical difficulties and appreciable limitations in its applicability. Nevertheless this method has attracted the attention of the Rome school, which has been reflected in papers devoted to the general discussion of emission spectra [155,156], the consideration of luminescence spectra of chromium(III) complexes of sulphur-containing ligands [157] and ethylenediaminetetra-acetic acid [158], platinum(II), [159,160] platinum(IV), [161] and manganese(II) [162] complexes, as well as certain instances of energy transfer to the centres responsible for luminescence or between these centres [163].

Mention should be made in this section also of research in the photochemistry of coordination compounds [mainly chromium and chromium(III) complexes], which is directly related to the study of luminescence spectra. The formation of the same preceding state—an excited ligand field or charge-transfer state—is necessary for both processes—a photochemical reaction or luminescence. As a result, the data obtained with the aid of the two methods supplement each other and thus make it possible to describe more accurately the excited states of metal complexes. The first studies were performed jointly with two leading groups in the field of inorganic photochemisty—those of Schläfer (emeritus Professor at Frankfurt) [164] and Prof. Adamson in Los Angeles [165,166]. These studies initiated original research into the mechanisms of photochemical substitution reactions involving certain chromium(III) complexes [167,168], particularly the *trans*-disubstituted complexes $[CrA_4XY]$, in which isomerisation and (or) substitution takes place [169,170]. Among other studies [171,172], those on the mechanisms of energy transfer from certain sensitisers in reactions of chromium(III) complexes are of special interest [173,174].

VII. VIBRATIONAL SPECTROSCOPY

The method is used mainly as an auxiliary procedure in the determination of structures or in order to test theories of bonding in coordination compounds. A number of early studies were devoted to the influence of the ligand field on the bond vibration frequencies in the molecule of the complex and in the ligands. In order to account for the vibration frequency shift in coordinated water molecules [175,176] and NH_4^+, [177,178] and BH_4^- ions in crystals [179], the method of perturbation theory was used. The normal coordinates have been analysed for certain cyano-complexes [180], carbonyls [180], and other coordination compounds.

Later, interest was concentrated on empirical problems associated with developing synthetic studies. For example, infrared spectroscopic data for nitroketone [181,182], dithio- and perthio-carboxylate [183-185], and a number of other complexes [186,187] have been published together with descriptions of the syntheses of the complexes and their other structural properties. In particular, investigations on nitroketone complexes began with the study of the infrared spectra of free nitroacetone and nitroacetophenone, the band assignments in the spectra being confirmed by the isotopic shifts for certain deuterated analogues [188]. Among metal complexes, copper(II) bis(nitroacetophenonate) has been most thoroughly investigated, because the simple structure of its crystal lattice permits a more accurate calculation [189]. In further investigations of nitroacetophenonates of other bivalent transition metals, copper(II) bisnitroacetonate, and certain univalent metal dinitroacetonates, satisfactory evidence was obtained for the delocalisation of the charge over the chelate rings and the influence of substituents [190].

The dithiobenzoates ($C_6H_5-CSS^-$ = dtb$^-$), dithiophenylacetates ($C_6H_5-CH_2-CSS^-$ = dtpa$^-$), dithioacetates (H_3C-CSS^- = dtac$^-$), and perthiobenzoates ($C_6H_5-CS_2S^-$ = dtbD$^-$) of certain bivalent and tervalent transition metals have been particularly thoroughly investigated. These investigations were associated with the problem of the assignment of the intense stretching vibration bands due to C–S, S–S, and other bonds in the chelate rings, for which there are contradictory literature data. Final conclusions were reached in experiments with deuteration, the observation of splittings in the spectra of crystals, and in certain instances with the aid of polarised infrared spectra of thin films [184,185].

VIII. ELECTROCHEMISTRY

As in other Italian universities, the scientists at Rome showed a deep interest in electrochemistry even before the war, particularly in polarographic studies on complexes [1,191]. Recently, the polarography of coordination compounds in an aqueous medium has been used to study the kinetics of the decomposition of $[Mn(C_2C_4)_3]^{3-}$ [192] and of complex formation in the system comprising copper(II) and polydentate amines [193-195] and in the study of the behaviour of certain organic ligands such as heterocyclic

nitrogen-containing bases[196,197] or dithiocarboxylates[198] at electrodes and of the polarographic properties of molybdenum(V)[199] and molybdenum(III).[200] However, polarography in aqueous solutions is at present being displaced by other methods, which are more powerful and are more widely applicable in the chemistry of coordination compounds: on the one hand, polarography in non-aqueous solvents and, on the other, pulsed electrolysis, particularly chronopotentiometry.

Polarography in non-aqueous solvents is used to study compounds which are insoluble or undergo decomposition in water. Furthermore, it is used in investigations involving protic and aprotic systems more or less similar to water. As regards water-insoluble compounds, aromatic disulphide–mercaptan systems have been studied in benzene–methanol mixtures, while related ligands of the type of dithiocarboxylates have been studied in water, acetonitrile (AN), and propylene carbonate (PC).[198] They were reduced to polymeric thioaldehydes, which, however, undergo certain side reactions.

Among metal complexes which do not dissolve in water without decomposition, the sandwich aromatic complexes of chromium have been studied in benzene–methanol mixtures, where the Cr^0/Cr^+ redox process approaches closely polarographic reversibility and is sensitive to the influence of substituents in aromatic ligands[202-205]. The tetrahedral transition metal halide complexes $[MX_4]^{2-}$ are fully hydrolysed in water, but can be investigated either in dimethylformamide[206,207] or in acetonitrile[208]. The properties of copper(II) complexes, which react with mercury at the electrode but exhibit normal properties at a platinum microelectrode, are of special interest[207,208].

In studies on polarography, continued at the present time and associated with synthetic research, the most suitable solvents proved to be acetonitrile and propylene carbonate. Dithiocarboxylate ligands and complexes have been investigated in propylene carbonate[198], while the properties of halogenomercury complexes[209] and mixed halogenophosphinecobalt(II) complexes[210,211] have been investigated in acetonitrile. A particular advantage of acetonitrile as a solvent is that it can be used simultaneously in both polarographic and potentiometric studies (the latter with Mo or W indicator electrodes), as well as spectrophotometric measurements. The joint use of the three methods enumerated makes it possible to describe quantitatively the complex equilibrium established in the systems mentioned above, incorporating mercury and cobalt complexes[209-212].

The limited applicability of the usual polarography led investigators to employ in many instances other electrochemical methods in order to investigate electrode processes involving metal complexes. The most successful attempt was that undertaken at the Rome school to employ pulsed d.c. electrolysis or transitometry. Catalytic reduction reactions of metal complexes have been studied both experimentally {for example in the $[Ni(CN)_4]^{2-}$ system}[213] and theoretically. For this purpose, a relation was established between the transfer time and the kinetic parameters for certain complex catalytic systems[214,215] and electrolytic reduction was studied after reversing the current[216].

The dependence of the current density on the concentrations of ligands and complexes has been determined with the aid of another important parameter, measured in pulsed d.c. electrolysis (the initial reduction potential) by recording the voltage–current characteristics for a non-polarised current. The parameter is used to obtain information about the mechanisms of the electrode reactions of certain metal complexes[217], for example, the electrode reactions of cadmium(II) and zinc[218], nickel(II) and copper(II),[219,220] and iron(II) and iron(III),[221] and especially in the study of ligand and (or) proton association or dissociation reactions in the bulk of the solution before discharge at the electrode. The method suffers from limitations, particularly in the case of very high rates of charge transfer at the electrode. Despite this, it has been used in many studies and has made it possible to identify a number of interesting electrochemically active complexes, frequently different from the compounds formed at equilibrium in solution[218-221].

IX. OTHER METHODS

The magnetic resonance methods have usually been employed as auxiliary procedures in relation to the more common methods, most of which have already been described in preceding sections. From the standpoint of microwave spectroscopy, studies on nuclear quadrupole resonance (NQR) of the halogens in halogeno-complexes, for example NQR of chlorine in certain crystalline tetrachloroureas, are of special interest[222,223].

Proton magnetic resonance has been used to confirm conclusions concerning the stereochemistry and reactivity of certain sulphur-containing complexes and the corresponding ligands. Dithio-, perthio-, and mixed dithio-perthio-complexes of transition metals may be identified with the aid of NMR and their interconversions may be followed[224]. The preferred conformations of certain substituted thioureas, both in the free state and as part of cobalt and zinc complexes, have been determined, which involved calculations on theoretical models of the corresponding structures[225-227]. The knowledge of conformation assisted in its turn in the elucidation of the contribution and role of hydrogen bonds, both intermolecular and intramolecular, which may be formed in metal–urea complexes in large numbers[226,227]. The conclusions reached have been confirmed by infrared spectroscopic data[82] and by X-ray diffraction[83,228]. In particular, it was shown that, for certain pseudotetrahedral dichlorobis(substituted urea)–zinc and –cobalt(II) complexes, the formation of intermolecular hydrogen bonds leads to chain polymerisation and that the resulting structures resemble to some extent the regular arrangements of polypeptide chains[83,228].

Photoelectron spectroscopy has been used on an increasing scale in research by the Rome school in recent years. The possibility of employing X-ray electronic spectroscopy in inorganic chemistry is still controversial as regards the validity of the measured ionisation energies the role of the effects of the solid phase in the determination of corrections to the results, and the factors influencing the true ionisation energy. Despite this, there is no doubt that the method has considerable potential possibilities for both analytical and structural research.

In the present author's studies attention was concentrated on certain aspects of the chemistry of complexes. X-Ray electronic spectroscopy makes it possible (to a greater extent than other methods) to determine the degrees of oxidation of two elements in certain rhodium–molybdenum heteropolyacids[229]. As regards molecular systems containing atoms in a common oxidation state, we investigated certain nickel(II) complexes of dithiocarbazinic acid $H_2N-NH-CSSH$ and its derivatives as well as the corresponding free ligands. These are ambident ligands i.e. contain several potential electron donors. Since the

degree of their oxidation is known, the change in electron binding energy yields information about the overall atomic charge—a quantity which is of fundamental importance for theoretical coordination chemistry, but is rarely susceptible to direct experimental determination. We were thus able to distinguish electron-donating atoms involved and not involved in complex formation and to obtain a schematic distribution of atomic charges along the complex of the complex[230]. Chromium(II) complexes, metal nitrosyls (particularly rhenium nitrosyls), and platinum acetylides have also been investigated by X-ray electronic spectroscopy.

Photoelectron spectroscopy with excitation by ultraviolet light yields more detailed information about the ionisation energies of valence orbitals. A significant limitation of this method is the requirement that the molecules investigated must be in vapour phase. Despite this limitation, the method has found extensive applications in coordination chemistry, where it can yield more extensive and more detailed information about the sequence of energies and the nature of the valence orbitals than the usual methods. The systems investigated in Rome include fluorinated sulphur-containing complexes, mainly perfluorodithiocarboxylates and the corresponding ligands [231], difluorodithiophosphates [232], and particularly thio- and dithio-derivatives of metal β-diketonates, such as nickel(II) bis(dithioacetylacetonate) and similar volatile nickel(II), cobalt(II), copper(II), and zinc complexes [233]. The existence of *d* orbitals adjoining or mixed with ligand orbitals, which differs from the traditional idea of clearly defined, separate, and partly filled electron shells in transition metal complexes, has been observed in these compounds.

X. APPLIED RESEARCH

Although applied research in the Rome school has not been of the type of systematic actively developing investigations, studies have been made on certain systems which are of potential or real applied interest, mainly catalytically active complexes and models for organic catalysis.

Studies of this kind were begun at the end of the 1950's, in collaboration with research workers of Natta's group in Milan in connection with the extensive applications of the Ziegler–Natta catalysts for the polymerisation of olefins. The first attempts were directed towards the elucidation of the structures of the active products of the reactions between transition metal halides (or acetylacetonates) and aluminium alkyls. For example, the formation of labile Cr(O) compounds was established in the reaction between $Cr(acac)_3$ and $AlEt_3$.[234,235] Subsequent investigations were devoted to the determination of the catalytic activities of certain Ziegler–Natta catalysts of the polymerisation reactions of acetylenic hydrocarbons [236–240]. It was found that monosubstituted acetylenes are converted into a mixture of symmetrical and asymmetric trisubstituted benzene derivatives. The yield of aromatic trimers usually depended on the catalyst : cocatalyst ratio. However, when different monomers were employed, the maximum yield did not correspond to the same catalyst : cocatalyst ratio. Linear polymers were also sometimes investigated.

Studies have been likewise carried out on other catalytic systems in order to find simpler reaction conditions. In fact, when catalysts of the Ziegler–Natta type are used, oxygen and water must be completely absent from the system. It was found that triphenylphosphinenickel complexes act as polymerising agents even when the reaction is carried out in solvents containing water and in air [241,242].

In the course of these investigations it was observed that the complex $(n\text{-}Bu_3P)_2NiBr_2$ is a very active catalyst for the trimerisation of α-hydroxyacetylenes having the general formula $HC{\equiv}C{-}\overset{\overset{OH}{|}}{C}{-}R$ (R′ below), pure 1,3,5-trisubstituted benzene derivatives being obtained in very high yields. Asymmetric isomers were not found in the reaction mixture [243].

In order to elucidate the role of transition metals in the mechanisms of catalytic reactions, a series of platinum complexes of bis(triphenylphosphines) were synthesised [244,245] and their catalytic activity was investigated in the polymerisation of phenylacetylene and 2-methylbut-3-yn-2-ol [246,247]. In the presence of platinum complexes monosubstituted alkynes were converted into linear polymers. Complexes having the general formula $[(C_6H_5)_3P]_2Pt(C{\equiv}C{-}R)_2$, containing the monomer linked by a σ bond to the platinum atom, were identified and isolated from the crude reaction mixture. These complexes may in fact be the active intermediates in the polymerisation reaction. There is evidence that the polymer chain grows as a result of the insertion of the monomer molecule in the Pt–C σ bond.

REFERENCES

1. G. Sartori, Gazzetta, 64, 3 (1934).
2. G. Sartori, Gazzetta, 64, 17 (1934).
3. V. Caglioti, Gazzetta, 66, 688 (1936).
4. G. Sartori, Gazzetta, 66, 717 (1936).
5. F. E. Ilse and H. Hartmann, Z. phys. Chem., 197, 239 (1951).
6. H. Bethe, Ann. Physik, 5, 3, 133 (1929).
7. J. H. Van Vleck, J. Chem. Phys., 7, 61 (1939).
8. H. Hartmann, C. Furlani, and A. Burger, Z. phys. Chem., 9, 62 (1956).
9. H. Hartmann and C. Furlani, Z. phys. Chem., 9, 162 (1956).
10. C. Furlani, Z. phys. Chem., 10, 291 (1957).
11. C. Furlani, Gazzetta, 87, 371 (1957).
12. C. Furlani and G. Sartori, Gazzetta, 87, 380 (1957).
13. C. Furlani and G. Morpurgo, Univ. Trieste, Facolta di Scienze, Pubbl. Istituto Chimico, No. 21 (1958).
14. C. Furlani and G. Sartori, J. Inorg. Nuclear Chem., 8, 126 (1958).
15. C. Furlani, Atti Accad. Naz. Lincei, Classe Sci., 28, 836 (1960).
16. C. Furlani and A. Donda, J. Inorg. Nuclear Chem., 19, 51 (1961).
17. C. Furlani and G. Morpurgo, Z. phys. Chem., 28, 93 (1961).
18. C. Furlani, E. Cervone, and V. Valenti, J. Inorg. Nuclear Chem., 25, 159 (1963).
19. C. Furlani and G. Morpurgo, Theor. Chim. Acta, 1, 102 (1963).
20. C. Furlani, Gazzetta, 92, 123 (1962).
21. F. Stefani, C. Furlani, and E. Semprini, Gazzetta, 101, 878 (1971).
22. C. Furlani, Coord. Chem. Rev., 3, 141 (1968).
23. F. Stefani and C. Furlani, Ricerca Sci., 39, 598 (1969).
24. A. Sgamellotti, P. Porta, and E. Cervone, Ricerca Sci., 38, 1223 (1968).
25. "The Proceedings of the Venice Symposium on Theoretical Aspects of Inorganic Chemistry", Coord. Chem. Rev., 2, 1 (1967).

26. G. Ciullo, C. Furlani, and A. Sgamellotti, J. Chem. Soc. A, 1299 (1971).
27. G. Ciullo, E. Semprini, and A. Sgamellotti, Gazzetta, 102, 1000 (1972).
28. G. Ciullo, C. Furlani, and A. Sgamellotti, Proc. XV Int. Conf. Coord. Chem., Moscow, 1973, p. 24.
29. F. Stefani, Gazzetta, 104 (1974), in the press.
30. C. Furlani, A. Sgamellotti, and F. Magrini, Rend. Accad. Naz. Lincei, Classe Sci., 41, 332 (1966).
31. M. Bonamico, G. Dessy, and V. Fares, Chem. Comm., 1106 (1969).
32. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, Proc. Ital.-Yugoslav. Cryst. Conf., Trieste, 1973.
33. P. Porta, A. Sgamellotti, and N. Vinciguerra, Inorg. Chem., 7, 2625 (1968).
34. P. Porta, A. Sgamellotti, and N. Vinciguerra, Inorg. Chem., 10, 541 (1971).
35. A. Sgamellotti, C. Furlani, and F. Magrini, J. Inorg. Nuclear Chem., 30, 2655 (1968).
36. G. Ciullo, C. Furlani, L. Sestili, and A. Sgamellotti, Inorg. Chim. Acta, 5, 489 (1971).
37. A. A. G. Tomlinson and C. Furlani, J. Chem. Soc., Dalton Trans., 1420 (1974).
38. A. A. G. Tomlinson, J. Chem. Soc. A, 1409 (1971).
39. C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, Chem. Comm., 1046 (1969).
40. C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, J. Chem. Soc. A, 2929 (1970).
41. L. Gastaldi, P. Porta, and A. A. G. Tomlinson, J. Chem. Soc., Dalton Trans., 1424 (1974).
42. L. Gastaldi, P. Porta, and A. A. G. Tomlinson, Proc. Ital. Yugoslav. Cryst. Conf., Trieste, 1973.
43. M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, Acta Cryst., 19, 619 (1965).
44. M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, Acta Cryst., 19, 886 (1965).
45. M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, Acta Cryst., 19, 898 (1965).
46. C. Furlani, E. Cervone, and F. Diomedi Camassei, Inorg. Chem., 7, 265 (1968).
47. E. Cervone, F. Diomedi Camassei, M. L. Luciani, and C. Furlani, J. Inorg. Nuclear Chem., 31, 1101 (1969).
48. M. Bonamico and G. Dessy, J. Chem. Soc. A, 264 (1971).
49. M. Bonamico and G. Dessy, Chem. Comm., 1114 (1967).
50. C. Cauletti and E. Cervone, J. Inorg. Nuclear Chem., 35, 593 (1973).
51. C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, Proc. 13th Int. Conf. Coord. Chem., Zakopane, 1970, Vol. 1, p. 269.
52. C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, J. Inorg. Nuclear Chem., 33, 3815 (1971).
53. C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, Proc. 4th Nat. Congr. Inorg. Chem., Venice, 1971, Abstract B5.
54. C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, Inorg. Nuclear Chem. Letters, 7, 981 (1971).
55. P. Porta and L. Gastaldi, Acta Cryst. (A), Suppl., 79 (1972).
56. L. Gastaldi and P. Porta, Cryst. Struct. Comm., 3, 467 (1973).
57. D. Gattegno and A. M. Giuliani, J. Inorg. Nuclear Chem., 36 (1974).
58. D. Gattegno and A. M. Giuliani, Inorg. Nuclear Chem. Letters, 9, 1179 (1973).
59. G. Mattogno, A. Monaci, and F. Tarli, Proc. 14th Int. Conf. Coord. Chem., Zakopane, 1970, p. 286.
60. G. Mattogno, A. Monaci, and F. Tarli, Proc. 5th Nat. Congr. Inorg. Chem., Taormina, 1972, Abstract A32.
61. F. Tarli, A. Monaci, and F. Monacelli, unpublished data.
62. A. Monaci and F. Tarli, unpublished data.
63. C. Battistoni, A. Monaci, G. Mattogno, and F. Tarli, Inorg. Nuclear Chem. Letters, 7, 981 (1971).
64. A. Monaci and F. Tarli, Inorg. Nuclear Chem. Letters, 9, 443 (1973).
65. P. V. Gogorishvili and T. M. Khonelidze, Russ. J. Inorg. Chem. Engl. Ed., 6, 663 (1961).
66. A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, Z. Krist., 122, 17 (1965).
67. J. Slivnik, A. Rihar, and B. Sedij, Monatsh., 98, 200 (1967).
68. C. Furlani and M. L. Luciani, Inorg. Chem., 7, 1586 (1968).
69. C. Furlani, A. Flamini, A. Sgamellotti, C. Bellitto, and O. Piovesana, J. Chem. Soc., Dalton Trans., 2404 (1973).
70. M. Bonamico, G. Dessy, and V. Fares, Chem. Comm., 324 (1969).
71. M. Bonamico and G. Dessy, Chem. Comm., 483 (1968).
72. C. Furlani, O. Piovesana, and A. A. G. Tomlinson, J. Chem. Soc., Dalton Trans., 212 (1972).
73. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, Cryst. Struct. Comm., 2, 201 (1973).
74. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, Acta Cryst., A28, 517 (1972).
75. M. Bonamico, G. Dessy, and V. Fares, Chem. Comm., 697 (1969).
76. M. L. Luciani and C. Furlani, Inorg. Chem., 10, 2614 (1971).
77. C. Furlani, M. L. Luciani, and R. Candori, J. Inorg. Nuclear Chem., 30, 3121 (1968).
78. A. Flamini, C. Furlani, and O. Piovesana, J. Inorg. Nuclear Chem., 33, 1841 (1971).
79. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, J. Chem. Soc. A, 3191 (1971).
80. E. Cervone, P. Cancellieri, and C. Furlani, J. Inorg. Nuclear Chem., 30, 2431 (1968).
81. O. Piovesana and C. Furlani, J. Inorg. Nuclear Chem., 30, 1249 (1968).
82. O. Piovesana and C. Furlani, J. Inorg. Nuclear Chem., 32, 879 (1970).
83. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, J. Chem. Soc. A, 3195 (1971).
84. T. Tarantelli and C. Furlani, J. Chem. Soc. A, 1717 (1968).
85. T. Tarantelli and C. Furlani, Chim. Ital., 100, 1012 (1970).
86. T. Tarantelli and C. Furlani, Chim. Ital., 100, 1076 (1970).
87. C. Furlani and T. Tarantelli, Inorg. Nuclear Chem. Letters, 2, 391 (1966).
88. C. Furlani, T. Tarantelli, L. Gastaldi, and P. Porta, J. Chem. Soc. A, 3778 (1971).
89. L. Gastaldi and P. Porta, Gazzetta, 101, 641 (1971).
90. P. Porta, T. Tarantelli, L. Gastaldi, and C. Furlani, Inorg. Chim. Acta, 5, 616 (1971).
91. T. Tarantelli, P. Riccieri, and C. Furlani, J. Inorg. Nuclear Chem., 31, 3585 (1969).
92. G. Ciullo, T. Tarantelli, and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 49, 111 (1970).

93. C. Furlani, T. Tarantelli, and P. Riccieri, J. Inorg. Nuclear Chem., 33, 1389 (1971).
94. T. Tarantelli and C. Furlani, J. Inorg. Nuclear Chem., 34, 999 (1972).
95. T. Tarantelli, J. Chem. Soc., Dalton Trans., 837 (1974).
96. C. Furlani and T. Tarantelli, Gazzetta, 103, 951 (1973).
97. M. Bonamico, I. Collamati, C. Ercolani, and G. Dessy, Chem. Comm., 654 (1967).
98. D. Attanasio, I. Collamati, and C. Ercolani, J. Chem. Soc., Dalton Trans., 772 (1972).
99. R. Astolfi, I. Collamati, and C. Ercolani, J. Chem. Soc., Dalton Trans., 2238 (1973).
100. D. Attanasio, I. Collamati, C. Ercolani, and G. Rotilio, J. Chem. Soc., Dalton Trans., 2242 (1973).
101. I. Collamati and C. Ercolani, J. Chem. Soc. A, 1537 (1969).
102. I. Collamati and C. Ercolani, J. Chem. Soc. A, 1541 (1969).
103. D. Attanasio, I. Collamati, and C. Ercolani, J. Chem. Soc. A, 2516 (1971).
104. I. Collamati, J. Chem. Soc. A, 2522 (1971).
105. S. Allessandrini, I. Collamati, and C. Ercolani, J. Chem. Soc., Dalton Trans., 2409 (1973).
106. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, Proc. Ital.-Yugoslav. Cryst. Conf. Trieste, 1973.
107. C. Furlani, G. Mattogno, A. Monaci, and F. Tarli, Inorg. Chim. Acta, 4, 187 (1970).
108. C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, J. Inorg. Nuclear Chem., 32, 2313 (1970).
109. [No. Ref. 109 given in Russian (Ed. of Translation)].
110. C. Furlani and G. Giullo, J. Inorg. Nuclear Chem., 1167 (1965).
111. E. Cervone and C. Furlani, Ann. Chim. (Italy), 51, 838 (1961).
112. E. Cervone, Ann. Chim. (Italy), 52, 1167 (1962).
113. C. Furlani and E. Zinato, Z. anorg. Chem., 351, 210 (1967).
114. C. Furlani and O. Piovesana, Mol. Phys., 9, 341 (1965).
115. O. Piovesana and C. Furlani, Inorg. Nuclear Chem. Letters, 3, 535 (1967).
116. C. Ercolani, C. Neri, and P. Porta, Inorg. Chim. Acta, 1, 415 (1967).
117. C. Ercolani and C. Neri, J. Chem. Soc. A, 1715 (1967).
118. C. Ercolani, C. Neri, and G. Sartori, J. Chem. Soc. A, 2123 (1968).
119. C. Ercolani, J. V. Quagliano, and L. M. Vallarino, Inorg. Chim. Acta, 3, 421 (1969).
120. C. Ercolani, J. V. Quagliani, and L. M. Vallarino, Chem. Comm., 1094 (1969).
121. C. Ercolani, J. V. Quagliano, and L. M. Vallarino, Inorg. Chim. Acta, 7, 413 (1973).
122. V. Caglioti, C. Furlani, G. Dessy, and C. Ibarra, Gazzetta, 92, 1276 (1962).
123. C. Furlani and E. Cervone, Ann. Chim. (Italy), 52, 564 (1962).
124. L. Sestili and C. Furlani, J. Inorg. Nuclear Chem., 32, 1997 (1970).
125. L. Sestili, C. Furlani, and G. Festuccia, J. Inorg. Nuclear Chem., 4, 542 (1970).
126. C. Furlani and L. Sestili, Ricerca Sci., 36, 819 (1966).
127. F. Aprile, V. Caglioti, and G. Illuminati, J. Inorg. Nuclear Chem., 21, 300, 325 (1962).
128. F. Monacelli, F. Basolo, and R. G. Pearson, J. Inorg. Nuclear Chem., 24, 1241 (1962).
129. V. Carunchio and G. Illuminati, J. Inorg. Nuclear Chem., 28, 2693 (1966).
130. F. Monacelli, J. Inorg. Nuclear Chem., 29, 1079 (1967).
131. G. Illuminati and F. Monacelli, J. Inorg. Nuclear Chem., 29, 1265 (1967).
132. F. Monacelli, Inorg. Chim. Acta, 1, 271 (1967).
133. V. Carunchio, G. Illuminati, and G. Ortaggi, Inorg. Chem., 6, 2168 (1967).
134. F. Monacelli and E. Viel, Inorg. Chim. Acta, 1, 467 (1967).
135. F. Monacelli, Inorg. Chim. Acta, 2, 263 (1968).
136. E. Borghi and F. Monacelli, Inorg. Chim. Acta, 5, 211 (1971).
137. E. Borghi, F. Monacelli, and T. Prosperi, Inorg. Nuclear Chem. Letters, 6, 667 (1970).
138. T. W. Swaddle and D. R. Stranks, J. Amer. Chem. Soc., 94, 8357 (1972).
139. F. Monacelli, Ricerca Sci., 37, 777 (1967).
140. F. Monacelli, Ricerca Sci., 37, 781 (1967).
141. F. Monacelli and S. Viticoli, Inorg. Chim. Acta, 7, 231 (1973).
142. G. Illuminati and F. Maspero, Ricerca Sci., 38, 544 (1968).
143. F. Maspero and G. Ortaggi, in the press (1974).
144. M. Casula, G. Illuminati, and G. Ortaggi, Inorg. Chem., 11, 1062 (1972).
145. B. Floris, G. Illuminati, and G. Ortaggi, Tetrahedron Letters, 4, 269 (1972).
146. B. Floris, G. Illuminati, P. E. Jones, and G. Ortaggi, Coord. Chem. Rev., 8, 39 (1972).
147. B. Floris and G. Ortaggi, J. Organometall. Chem., 50, 33 (1973).
148. G. Cerichelli, B. Floris, G. Illuminati, and G. Ortaggi, unpublished data.
149. C. Furlani, E. Cervone, F. Calzona, and B. Baldanza, Theor. Chim. Acta, 7, 375 (1967).
150. C. Furlani, A. Sgamellotti, F. Magrini, and D. Cordischi, J. Mol. Spectroscopy, 24, 270 (1967).
151. A. A. G. Tomlinson and C. Furlani, Inorg. Chim. Acta, 3, 487 (1969).
152. A. A. G. Tomlinson, C. Bellitto, O. Piovesana, and C. Furlani, J. Chem. Soc., Dalton Trans., 350 (1972).
153. C. Bellitto, A. A. G. Tomlinson, and C. Furlani, J. Chem. Soc. A, 3267 (1971).
154. A. A. G. Tomlinson, C. Bellitto, and C. Furlani, J. Chem. Soc., Dalton Trans., in the press (1974).
155. C. Furlani, Coord. Chem. Rev., 1, 51 (1966).
156. G. Sartori, C. Furlani, and E. Cervone, Acta Chim. Acad. Sci. Hung., 29, 231 (1968).
157. P. Cancellieri, E. Cervone, C. Furlani, and G. Sartori, Z. phys. Chem., 62, 35 (1968).
158. R. Candori and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 44, 415 (1968).
159. L. Ancarani Rossiello and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 38, 207 (1965).
160. D. L. Webb and L. Ancarani Rossiello, Inorg. Chem., 10, 2213 (1971).
161. L. Ancarani Rossiello, J. Chem. Phys., 51, 5191 (1969).
162. C. Furlani, E. Cervone, and P. Cancellieri, Rend. Accad. Naz. Lincei, Classe Sci., 37, 446 (1964).

163. R. Candori and C. Furlani, Chem. Phys. Letters, 5, 153 (1970).
164. P. Riccieri and H. L. Schläfer, Inorg. Chem., 9, 727 (1970).
165. R. D. Lindholm, E. Zinato, and A. W. Adamson, J. Amer. Chem. Soc., 91, 1076 (1969).
166. A. W. Adamson, A. Chiang, and E. Zinato, J. Amer. Chem. Soc., 91, 5467 (1969).
167. E. Zinato, P. Riccieri, and A. W. Adamson, J. Amer. Chem. Soc., 96, 375 (1974).
168. E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, Inorg. Chem., 11, 746 (1972).
169. P. Riccieri and E. Zinato, Proc. 14th Int. Conf. Coord. Chem., Toronto, 1972, p. 252.
170. P. Riccieri and E. Zinato, Inorg. Chim. Acta, 7, 117 (1973).
171. E. Zinato and P. Riccieri, Inorg. Chem., 12, 1451 (1973).
172. E. Zinato and P. Riccieri, Inorg. Chem., 14, in the press (1974).
173. E. Zinato, P. Tulli, and P. Riccieri, J. Phys. Chem., 75, 3504 (1971).
174. P. Riccieri and E. Zinato, Z. phys. Chem., 79, 28 (1972).
175. G. Sartori and C. Furlani, Z. phys. Chem., 15, 336 (1958).
176. C. Furlani, Gazzetta, 88, 65 (1958).
177. V. Caglioti and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 24, 633 (1958).
178. V. Caglioti, M. Scrocco, and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 26, 625 (1959).
179. V. Caglioti and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 26, 147 (1959).
180. V. Caglioti, G. Sartori, and C. Furlani, J. Mol. Spectroscopy, 9, 337 (1962).
181. M. Maltese and C. Ercolani, J. Chem. Soc. B, 1147 (1970).
182. M. Maltese, unpublished data.
183. O. Piovesana, C. Furlani, A. Flamini, A. Sgamellotti, and C. Bellitto, Rend. Accad. Naz. Lincei, Classe Sci., in the press (1974).
184. M. Maltese, J. Chem. Soc., Dalton Trans., 2664 (1972).
185. M. Maltese, unpublished data.
186. M. Maltese and W. J. Orville-Thomas, J. Inorg. Nuclear Chem., 29, 2533 (1967).
187. F. Monacelli, G. Mattogno, D. Gattegno, and M. Maltese, Inorg. Chem., 9, 686 (1970).
188. M. Maltese, unpublished data.
189. M. Maltese, unpublished data.
190. M. Maltese, unpublished data.
191. G. Sartori, J. Inorg. Nuclear Chem., 8, 196 (1958).
192. C. Furlani and A. Ciana, Ann. Chim. (Italy), 47, 1081 (1957).
193. A. M. Giuliani, D. Gattegno, and A. Furlani, J. Electroanal. Chem., 18, 151 (1968).
194. D. Gattegno, A. M. Giuliani, and M. R. Imperatori, J. Electroanal. Chem., 24, 435 (1970).
195. D. Gattegno and A. M. Giuliani, Electrochim. Acta, 15, 203 (1970).
196. C. Furlani, "Contributi di Polarografia", Vol. 2, Suppl. to Ricerca Sci., 26, 103 (1956).
197. C. Furlani, S. Bertola, and G. Morpurgo, Ann. Chim. (Italy), 50, 858 (1960).
198. L. Sestili, Gazzetta, 102, 647 (1972).
199. O. Piovesana, Gazzetta, 99, 86 (1969).
200. A. Ciana and O. Piovesana, Rend. Accad. Naz. Lincei, Classe Sci., 41, 324 (1966).
201. G. Sartori and C. Furlani, "Contributi di Polarografia", Suppl. to Ricerca Sci., 26, 220 (1956).
202. C. Furlani and E. O. Fischer, Z. Electrochem., 61, 481 (1957).
203. C. Furlani and G. Sartori, Ricerca Sci., 28, 973 (1958).
204. C. Furlani, A. Furlani, and L. Sestili, J. Electroanal. Chem., 9, 140 (1965).
205. C. Furlani, Ricerca Sci., 36, 989 (1966).
206. A. Ciana and C. Furlani, Electrochim. Acta, 10, 1149 (1965).
207. L. Sestili, C. Furlani, A. Ciana, and F. Garbassi, Electrochim. Acta, 15, 225 (1970).
208. C. Furlani, L. Sestili, A. Ciana, and F. Garbassi, Electrochim. Acta, 12, 1393 (1967).
209. C. Furlani and L. Sestili, Ricerca Sci., 36, 819 (1966).
210. L. Sestili, C. Furlani, and G. Festuccia, Inorg. Chim. Acta, 4, 542 (1970).
211. L. Sestili and C. Furlani, J. Inorg. Nuclear Chem., 33, 503 (1971).
212. L. Sestili and C. Furlani, J. Inorg. Nuclear Chem., 32, 1997 (1970).
213. G. Sartori, C. Furlani, and G. Morpurgo, Z. Electrochem., 63, 588 (1959).
214. C. Furlani, "Contributi di Polarografia", Suppl. to Ricerca Sci., 29, 127 (1959).
215. C. Furlani, A. Furlani, and A. M. Giuliani, Rend. Accad. Naz. Lincei, Classe Sci., 37, 310 (1964).
216. C. Furlani and G. Morpurgo, J. Electroanal. Chem., 1, 351 (1960).
217. V. Caglioti, G. Sartori, C. Furlani, and A. Donda Furlani, Ricerca Sci., 32, 398 (1962).
218. C. Furlani and A. Donda Furlani, Ricerca Sci., 32, 411 (1962).
219. C. Furlani and A. Donda Furlani, Ricerca Sci., 32, 439 (1962).
220. A. Furlani, A. M. Giuliani, and C. Furlani, Rend. Accad. Naz. Lincei, Classe Sci., 37, 436 (1964).
221. C. Furlani, G. Morpurgo, and A. M. Giuliani, Ricerca Sci., 32, 449 (1962).
222. V. Caglioti, C. Furlani, F. Orestano, and F. M. Capece, Rend. Accad. Naz. Lincei, Classe Sci., 35, 10 (1963).
223. M. Bonamico, G. Dessy, C. Furlani, and F. M. Capece, Acta Cryst., B29, 1737 (1973).
224. A. M. Giuliani, Inorg. Nuclear Chem. Letters, 7, 1001 (1971).
225. D. Gattegno and A. M. Giuliani, J. Chem. Soc., Dalton Trans., 1399 (1973); 1646 (1973).
226. A. M. Giuliani, J. Chem. Soc., Dalton Trans., 497 (1972).
227. A. M. Giuliani, J. Chem. Soc., Dalton Trans., 41 (1973).
228. M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, J. Chem. Soc., Dalton Trans., 876 (1973).
229. A. La Ginestra, C. Ferragina, S. Correnti, L. Cicconetti, G. Mattogno, and C. Battistoni, Gazzetta, 103, 963 (1973).
230. C. Battistoni, M. Bossa, C. Furlani, and G. Mattogno, J. Electron Spectr. Rel. Phen., 2, 355 (1973).
231. A. Flamini, E. Semprini, and G. Condorelli, J. Electron Spectr. Rel. Phen., 4 (1974) (in the press).
232. A. Flamini and C. Furlani, J. Electron Spectr. Rel. Phen., 4 (1974) (in the press).
233. C. Cauletti and C. Furlani, J. Electron Spectr. Rel. Phen., 4 (1974) (in the press).

234. G. Sartori and G. Costa, Z. Electrochem., 63, 105 (1959).
235. G. Sartori, E. Cervone, A. Furlani, and I. Collamati, Ricerca Sci., 32, 385 (1962).
236. A. Furlani Donda, E. Cervone, and M. A. Biancifiori, Rec. Trav. Chim., 81, 585 (1962).
237. G. Stea and A. Donda Furlani, Ricerca Sci., 33, 609 (1963).
238. A. Donda Furlani and A. Guerrieri, Ricerca Sci., 34, 287 (1964).
239. G. Sartori, A. Furlani, and G. Variali, Chimica e Industria, 49, 357 (1967).
240. A. Furlani, G. Moretti, and A. Guerrieri, J. Polymer Sci., Polymer Letters, 5, 523 (1967).
241. A. Furlani and G. Moretti, J. Org. Chem., 31, 985 (1966).
242. D. Cordischi, A. Furlani, P. Bitchev, M. V. Russo, and P. Carusi, Gazzetta, 101, 526 (1971).
243. P. Bitchev, A. Furlani, and G. Sartori, Gazzetta, 104, in the press (1974).
244. I. Collamati and A. Furlani, J. Organometallic Chem., 17, 457 (1969).
245. A. Furlani, P. Bitchev, and M. V. Russo, J. Organometallic Chem., 29, 321 (1971).
246. A. Furlani, I. Collamati, and G. Sartori, J. Organometallic, Chem., 17, 463 (1969).
247. A. Furlani, P. Bitchev, P. Carusi, and M. V. Russo, J. Polymer Sci., Polymer Letters, 9, 19 (1971).

Institute of General and
Inorganic Chemistry,
Rome University

Laboratory of Coordination
Compounds of the National
Research Council of Italy