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Metal Chelates of Heterocyclic Nitrogen Containing Ketones.
I. 2-Picolylphenyl and 2-Quinaldylphenyl Ketonate Metal Complexes

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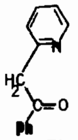
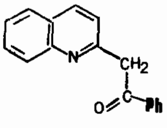
The reaction of 2-picolyl and 2-quinaldylphenyl ketones with nickel(II), cobalt(II) and copper(II) ions was investigated. Magnetic and spectral data were used to determine the structure of the complexes. Both ketones react with Cu(II), forming distorted tetrahedral complexes, while the Ni(II) ion forms a square planar complex with a 2-picolylphenyl ketone and a tetrahedral complex with a 2-quinaldylphenyl ketone. The reaction with the Co(II) ion gave a high-spin tetrahedral complex with a 2-picolylphenyl ketone and a five coordinate polymeric type with a 2-quinaldylphenyl ketone. The solution spectra of the complexes as well as their base adducts were also investigated.

Introduction

Schiff base metal complexes form stereochemical interconvertible compounds [1–6]. In these types of compounds, very small differences in the electronic properties or steric requirements of the ligands would result in the formation of complexes with different configurations [3, 4]. The most novel chelating ligands which have similar properties are 2-picolylphenyl ketone (PPK) (I) and 2-quinaldylphenyl ketone (QPK) (II).



(I)



(II)

The coordination chemistry of these organic ligands is much less developed until now. These heterocyclic ketones give a nitrogen analog with the β-diketone-imine ligands. Compounds (I) and (II) have keto–enol tautomeric properties similar to the β-diketone [7]. Uhlemann *et al.* [8] studied qualitatively the 2-picolyl ketones as complexing agents with the first row transition elements. The 2-picolyl ketones used are 2-picolyl mesityl ketone, 2-picolyl-β-naphthyl ketone and 2-picolyl diphenyl ketone. The structures of these metal complexes were found to be in planar, tetrahedral or octahedral configurations based on the magnetic measurements at 288 °K. A complete investigation of the spectral properties of the solid complexes, as well as their solutions, has not been carried out to support such proposed configurations. In the present work, the Cu(II), Ni(II) and Co(II) complexes with ligands (I) and (II) were prepared; the isolated solid complexes were studied using magnetic measurements together with infrared and electronic absorption data. The solution spectra as well as their base adducts were also investigated.

Experimental

Preparation of the Ligands

2-Picolylphenyl ketone (PPK)

The ketone was prepared from methyl benzoate and 2-picolyl lithium under nitrogen, by the method of N. Goldberg *et al.* [9]. The crude product was fractionated in vacuum at 2 mmHg and the pure product was collected at 158 °C. Recrystallization from ligroin gave yellow needles with m.p 53–54 °C.

2-Quinaldylphenyl ketone (QPK) was prepared in 90% yield from 2-quinaldyl lithium and methyl benzoate in dry ether under nitrogen by the method of Goldberg and R. Levin [10]. The ketone was recrystallized from ethanol as orange crystals, m.p 118–119 °C.

Preparation of the Metal Complexes

Bis(2-picolylphenyl ketonato)Cu(II), $(PPK)_2Cu$

A solution of copper(II) acetate (0.01 mol) in 25 ml ethanol was refluxed for 10 minutes with 2-picolylphenyl ketone (0.02 mol) Brown crystals of copper complex were separated, filtered off, washed

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TABLE I. Analytical Data.

Compounds	Color	M.p. (°C)	N%	(Calcd)	M%	(Calcd)
$(PPK)_2Cu$	Brown	184	6.10	(6.15)	13.93	(13.94)
$(PPK)_2Ni$	Brown	188	6.20	(6.21)	12.76	(13.03)
$(PPK)_2Co$	Dark Green	196	6.30	(6.21)	12.98	(13.07)
$(QPK)_2Cu$	Olive Green	224	5.30	(5.04)	11.43	(11.44)
$(QPK)_2Ni$	Reddish–Brown	278	4.95	(5.08)	10.26	(10.66)
$(QPK)_2Co$	Orange–Red	298	4.90	(5.08)	10.47	(10.69)

TABLE II. Infrared Data.

Complex	ν CO, CN	ν C–C, C–N	ν C–C (st.) and ν C–H (bend.)
PPK	1680, 1625	1600	1460
$(PPK)_2Cu$	1620(S)	1580	1460
$(PPK)_2Ni$	1600	1590	1480
$(PPK)_2Co$	1607	1587	1497
QPK	1625	1580	1460
$(QPK)_2Cu$	1630, 1620	1580	1450
$(QPK)_2Ni$	1620, 1585	1570	1445
$(QPK)_2Co$	1630, 1624	1578	1460

with ethanol, crystallized from ether and dried *in vacuo* over P_2O_5.

Bis(2-quinaldylphenyl ketonato)Cu(II), $(QPK)_2Cu$

A solution of copper(II) acetate (0.01 mol) in 25 ml ethanol was refluxed with 2-quinaldylphenyl ketone (0.02 mol) in 20 ml ethanol for 40 minutes. The olive green crystals which separated were washed several times with ethanol and dried. The complex was soluble in acetonitrile, dimethyl formamide and pyridine, but sparingly soluble in chloroform.

Bis(2-picolylphenyl ketonato)Ni(II), $(PPK)_2Ni$

An ammoniacal solution (30 ml) of nickel(II) acetate (0.01 mol) was refluxed with 2-picolylphenyl ketone (0.02 mol) in ethanol for three hours. The nickel complex was separated as brown crystals, filtered off and washed with ether and dried *in vacuo* over P_2O_5. The complex was soluble in chloroform, acetonitrile, pyridine and dimethyl formamide.

Bis(2-quinaldylphenyl ketonato)Ni(II), $(QPK)_2Ni$

An ammoniacal solution of nickel(II) acetate (0.01 mol) in 25 ml ethanol was refluxed with 2-quinaldylphenyl ketone (0.02 mol) in ethanol for one hour. Reddish–brown crystals were separated, filtered, washed with ether and dried. The complex was soluble in acetonitrile, dimethyl formamide and pyridine, but sparingly soluble in chloroform.

Bis(2-picolylphenyl ketonato)Co(II), $(PPK)_2Co$

A solution of cobalt(II) acetate (0.01 mol) in 25 ml ethanol was refluxed for one hour with 2-picolylphenyl ketone (0.02 mol) in ethanol. A greenish color developed and dark green crystals of the cobalt complex were separated after three hours of refluxing. The crystals were filtered and dried over P_2O_5. The preparation was carried out under nitrogen and yielded the same products, which ruled out any oxidation to Co(III).

Bis(2-quinaldylphenyl ketonato)Co(II), $(QPK)_2Co$

A solution of cobalt acetate (0.01 mol) in ethanol was refluxed with 2-quinaldylphenyl ketone (0.02 mol) in ethanol for 45 minutes. Orange–red crystals were separated, then filtered out and washed with ether and dried *in vacuo* over P_2O_5. The complex was sparingly soluble in chloroform, but soluble in pyridine and acetonitrile.

Physical Measurements

Infrared spectra were measured using a Unicam S.P. 200 spectrophotometer. Samples were prepared at KBr discs. Major bands of the ligands and the complexes are given in Table II. Electronic absorption spectra were measured with Unicam S.P. 600 and S.P. 800 spectrophotometers. Nujol mull spectra were measured according to the method of Kleinberg [11]. The magnetic susceptibilities of the complexes were measured at 298 °K by the Gouy method. Mercury tetrathiocyanato cobalt(II) was used as a standard and the magnetic corrections were estimated by the method outlined by Figgis and Lewis [12].

Elemental Analysis

Copper, nickel and cobalt were determined titrimetrically with ethylenediammine tetraacetic acid (EDTA). Carbon, hydrogen, and nitrogen analyses were carried out at the Microanalysis Laboratory, Cairo University.

Results and Discussion

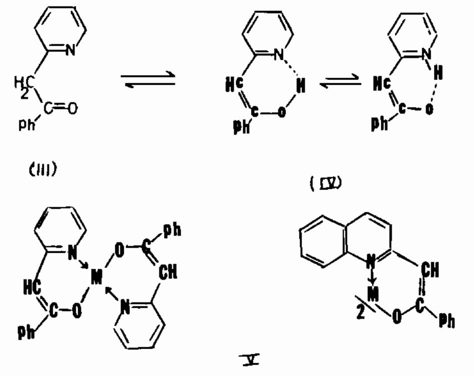
The heterocyclic monocarbonyl ligands can act as neutral didentate (I) or monobasic didentate ligands

TABLE III. Frequencies (ν, cm^{-1}), Extinction Coefficients (E.L. mol^{-1} cm^{-1} and Magnetic Moment of bis(2-phenylpicolyl ketonato)M(II) Complexes.

Compound	μ_{eff} (B.M.)	Medium	ν (E)
$(PPK)_2Cu$	1.80	Solid[a]	18,519(sh), 14,705, 13,699, 12,987(sh), 11,364
		$CHCl_3$	16,949(296), 15,625(230), 13,793(152), 13,158(132), 12,500(108), 11,628(86)
		Pyridine	18,518(sh), 14,705(b), 13,514(sh)
$(PPK)_2Ni$	0	Solid	13,333, 16,660, 19,230
		$CHCl_3$	13,699(43), 14,706(46), 16,129(56), 17,857(52)
		Pyridine	10,870, 13,888, 16,393(sh), 18,181
$(PPK)_2Co$	4.20	Solid	11,111, 15,600, 18,867
		$CHCl_3$	10,042(95), 14,925, 15,625(200)
		Pyridine	16,393(513), 14,706(363), 11,903(200)

[a] Nujol mulls, sh = shoulder, b = broad.

through enolization (IV). The coordination can take place in the enol form through the enolized oxygen and the nitrogen atom of the hetero ring, producing neutral-type chelates (V).



M = Cu(II), Ni(II), and Co(II)

The infrared spectra of the organic ligands, as well as their corresponding metal chelates, were measured as KBr discs. The positions of some of the most characteristic bands are listed in Table II. The spectra exhibited appreciable perturbations in the fundamental frequencies of the pyridine and quinaldine parts of the molecule.

The broad split band of the PPK was due to ν Co, CN at 1680 and 1625 cm^{-1} shifted to lower frequencies. It gave a strong single band in all the complexes. The metal complexes of both ligands showed similarities in their infrared spectra with pronounced shift in ν Co, CN indicating strong interaction by chelations through the enolized C···O and the nitrogen atom of the hetero ring. The decrease in the frequency shift could be attributed to the increase in the conjugation of the π-system of the ligands on coordination.

Electronic Spectra and the Structure of the Complexes – Copper(II) Complexes

Bis(2-picolylphenyl ketonato)Cu(II), $(PPK)_2Cu$

The nujol mull electronic spectrum of $(PPK)_2Cu$ exhibits four bands in the region 18,519, 14,705, 13,699 and 11,364 cm^{-1}. In addition, a weak shoulder at about 12,987 cm^{-1} was observed (Table III). The shape as well as the position of the bands could not account for the square planar structure which usually showed a broad band around 14,000–16,000 cm^{-1} [13]. However, the spectra of $(PPK)_2Cu$ in both the solid and $CHCl_3$ solution (Table III) are similar to the spectra reported for bis(t-butylsalicylideneaminato)Cu(II) which was found to be distorted tetrahedral [14]. For truly tetrahedral copper(II) complexes, crystal field predicts only one transition due to $^2T_2 \rightarrow {}^2E$ [15]. The effective magnetic moment of pseudo tetrahedral copper(II) complexes was found to be 1.9 to 2.0 B.M. [15], which was larger than the value found for $(PPK)_2Cu$ (μ_{eff} = 1.85 B.M.) The absorption spectrum in chloroform (Table III) exhibits three bands and two shoulders at 13,158 and 12,500 cm^{-1}. Also there is a weak band centered at 11,628 cm^{-1}. Therefore, the position and the extinction coefficient of the solution spectrum support the distorted tetrahedral structure for $(PPK)_2Cu$, which has already been shown to exist in the solid state.

Four coordinate copper(II) complexes are known to expand their coordination number to five or six by the reaction with Lewis bases such as pyridine, forming adducts. The formation of five or six coordinate adducts is governed by the ligand field strength of the equatorial donor ligand and by steric factors. The spectrum of $(PPK)_2Cu$ in pyridine (Table III) exhibits an intense split band around 14,705–13,514

TABLE IV. Frequencies (ν, cm^{-1}), Extinction Coefficient (E.L. mol^{-1} cm^{-1}) and Magnetic Moments of bis(2-phenylquinaldyl ketonato)M(II) Complexes

Compound	μ_{eff} (B.M.)	Medium	ν(E)
$(QPK)_2Cu$	2.20	Solid	18,519(sh), 15,873(b), 13,884(sh), 12,987, 11,628
		DMF	11,241(182), 12,889(90)
		Pyridine	17,870, 15,625(b), 13,514(sh), 12,821
$(QPK)_2Ni$	3.26	Solid	11,627, 13,888, 15,151, 17,544
		DMF	10,204(108), 12,270(sh), 13,698(115), 15,585(120)
		Pyridine	11,111, 12,500, 14,286, 17,544
$(QPK)_2Co$	4.59	Solid	11,400, 14,300
		DMF	11,364, 12,500(sh), 13,699, 14,925, 17,857
		CH_3CN	12,121, 13,986, 16,393, 18,181
		Pyridine	11,364, 12,048(sh), 12,987, 13,889, 16,949

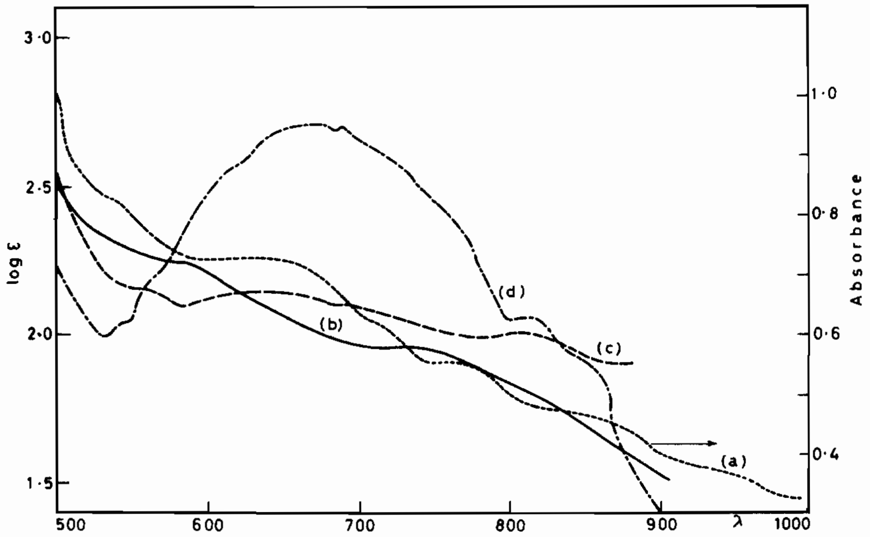


Figure 1. Electronic spectra of bis(2-quinaldylphenyl ketonato)Cu(II). (a) nujol mull spectra; (b) in pyridine; (c) in dimethyl formamide and (d) in acetonitrile.

cm^{-1} and also a less intense band at 12,340 cm^{-1}. Hathaway *et al.* [16, 17] reported that five coordinate trigonal bipyramidal copper(II) complexes are characterized by a single intense maximum around 12,000–14,000 cm^{-1}, while the square based pyramidal complexes exhibit a band at 14,500–15,750 cm^{-1} with a lower frequency shoulder at 11,000 cm^{-1}. Consequently, both the positions and intensities of the bands for the copper complex in pyridine are compatible with distorted square based pyramidal geometry.

Bis(2-quinaldylphenylketonato)Cu(II), (QPK)$_2$Cu

The mull spectrum of $(QPK)_2Cu$ (Table IV), showed bands at 15,873 with a shoulder at 13,889, 12,987 cm^{-1} and a weak broad band centered at 11,628 cm^{-1} (Fig. 1). The position of these bands and the observed magnetic moment (μ = 2.2 B.M.) were in accordance with the distorted tetrahedral stereochemistry.

The solution spectra of the complex in pyridine, dimethyl formamide (DMF) and acetonitrile were also measured (Table IV and Fig. 1). It is clear that the solution spectra of the complex are completely different from the one in the solid state which indicates strong interaction with the copper complex. The solution spectra in acetonitrile and pyridine are consistent with the square based pyramidal symmetry (C_{4v}). In dimethyl formamide the spectrum exhibits a broad band at 13,699 cm^{-1} and a high energy

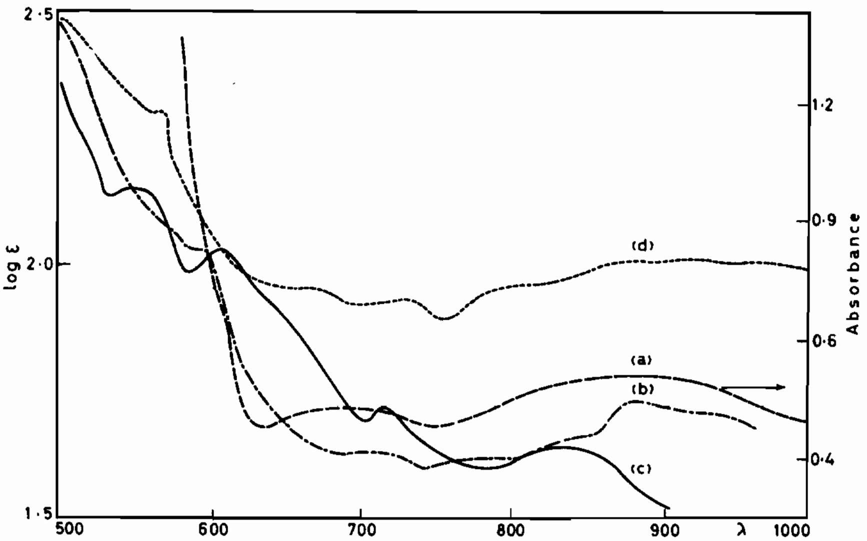


Figure 2. Electronic spectra of bis(2-quinaldylphenyl ketonato)Co(II). (a) nujol mull; (b) in pyridine; (c) in acetonitrile and (d) in dimethyl formamide.

charge transfer band at 17,090 cm^{-1} which suggests strong tetragonal distortion due to the interaction of the solvent.

Nickel(II) Complexes

The nickel(II) complexes of the heterocyclic ketones offer unique structural ligand effects in adopting stereochemical configurations due to the steric effect of the ligand [4].

Bis(2-picolylphenyl ketonato)Ni(II), (PPK)$_2$Ni

The nujol mull electronic spectrum of $(PPK)_2Ni$ (Table III) exhibits three bands at 13,333 (ν_1), 16,660 (ν_2) and 19,230 (ν_3) cm^{-1}. The magnetic moment ($\mu = 0$) indicates that the complex is a square planar. The solution spectrum in chloroform is similar to the nujol one and the lack of absorption in the near infrared region supports the singlet ground state $^1A_{1g}$, in accordance with the diamagnetic behavior. The spectrum in pyridine (Table III) shows three new bands characteristic of octahedral Ni(II) complexes which indicates strong interaction with the base forming dipyridinate adducts $(PPK)_2Ni\ PY_2$.

Bis(2-quinaldylphenyl ketonato)Ni(II), (QPK)$_2$Ni

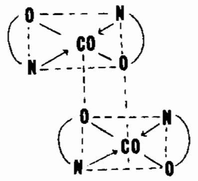
The reflectance spectrum of $(QPK)_2Ni$ exhibits a split band at 15,151 and 13,888 cm^{-1} besides a weak band at 11,627 cm^{-1}. According to the observed magnetic moment, μ_{eff} = 3.26 B.M., tetrahedral symmetry around the Ni(II) ion is suggested. It is interesting to note that the steric requirement of the 2-quinaldylphenyl ketone played a part in adopting the tetrahedral configuration. The more bulky the ligand, the more likely the adoption of the tetrahedral configuration becomes [4]. Typical examples of this effect were found among tertiary phosphine and bis-N-alkylsalicylaldimine [2]; in the latter case α-branched alkyl groups stabilized the tetrahedral form. Generally, all these complexes in solution give an equilibrium mixture of tetrahedral and square planar species [2, 19]. The solution spectra of $(QPK)_2Ni$ in pyridine and DMF show a strong interaction and formation of diadducts. The spectra showed the characteristic transition band of the tetragonal distorted octahedral nickel(II) complexes (Table IV).

Cobalt(II) Complexes

The complex is a high spin type. Its effective magnetic moment at room temperature is 4.20 B.M. The reflectance spectrum of the complex shows four bands in the region 10,000–20,000^{-1} (Table III). These data suggest tetrahedral arrangement around the central metal ion. Furthermore, the ligand field spectrum in chloroform consists of a maximum at 10,042 cm^{-1} (E = 95) and a split band in the ranges 15,625 (E = 200) and 14,442 cm^{-1} which is a typically tetrahedral spectral type [20]. In pyridine, there are bands at 11,905, 14,706 and 16,393 cm^{-1}. These values are different from those of typical six-coordinate dipyridinate Co(II) complexes which exhibit two bands around 10,000 and 17,800 cm^{-1}. An octahedral configuration for the base adducts may therefore be excluded, and a five coordinate configuration seems most probable as the one reported for the five coordinate Co(II) pyridine adducts [21]. It should be noted that the spectrum is characterized by high extinction coefficients which may suggest an equilibrium between the five coordinate monopyridinate adduct and the original tetrahedral complex.

Bis(2-quinaldylphenyl ketonato)Co(II), $(QPK)_2Co$

The effective magnetic moment of the complex at room temperature is equal to 4.59 B.M. which may suggest a tetrahedral configuration around the metal ion, but the reflectance spectrum (Fig. 2a) shows one broad band around 11,400 cm^{-1} and another one at 14,300 cm^{-1} which differ considerably from the spectra of high spin tetrahedral cobalt(II) complexes [20]. The complex is insoluble in all inert solvents and this can be attributed to its polymeric structure. It has been recently shown that the ability of the geometry of many metal complexes with Schiff bases gives rise to molecular configurations in solution, different from those in the solid state and conformational equilibrium between different forms takes place. Cobalt(II) and zinc(II) complexes with N-methyl salicylaldimine are mutually isomorphous; they exist a dimers in the solid state and have a coordination number five in a distorted trigonal bipyramidal environment [22]. Accordingly, bis(2-quinaldylphenyl ketonato)Co(II) may be considered to have a pentacoordinate structure, VI, of the type reported for bis(N-arylsalicylaldiminato)Co(II) complexes [22, 23].



(VI)

The electronic spectra in different solvents are given in Fig. 2 and Table IV. In acetonitrile the spectrum exhibits four bands; their positions and intensities suggest tetrahedral configuration in this solvent. In pyridine and DMF the spectra exhibit typical octahedral dibasic adducts.

References

1 a) R. H. Holm, G. W. Everett, Jr. and A. Chakravorty, Progr. Inorg. Chem., 7, 83 (1966). b) R. H. Holm, Accounts Chem. Res., 2, 307 (1970).

2 L. Sacconi, in R. L. Carlin (Ed.), "Transition Metal Chemistry", Marcel Dekker, New York, (1968) vol. 4, p. 199.

3 L. Sacconi, *Coord. Chem. Rev.*, *1*, 192 (1966).

4 E. Uhlig, *Coord. Chem. Rev.*, *10*, 227 (1973).

5 S. Yamada, *Coord. Chem. Rev.*, *2*, 83 (1967).

6 S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Corrd. Chem. Rev.*, *3*, 247 (1968).

7 J. Elgurco, Cl. Marzin, A. R. Katritzky and P. Linda, in "The Tautomerism of Heterocycles", Academic Press, New York, p. 190 (1976).

8 E. Uhlemann, *J. Prakt. Chem.*, *14*, 281 (1961).

9 N. N. Goldberg, L. Lloyd, B. Barkley and R. L. Levine, *J. Am. Chem. Soc.*, *73*, 4301 (1951).

10 N. N. Goldberg and R. Levine, *J. Am. Chem. Soc.*, *74*, 5217 (1952).

11 R. H. Lee, E. Griswold and J. Kleinberg, *Inorg. Chem.*, *3*, 1278 (1964).

12 B. N. Figgis and J. Lewis in "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins (Ed.), Interscience, New York (1960) p. 403.

13 A. B. P. Lever, in "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1968). p. 355.

14 L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

15 B. J. Hathaway and B. J. Billing, *Coord. Chem. Rev.*, *5*, 143 (1970).

16 B. J. Hathaway, R. J. Budly and P. Nicholls, *J. Chem. Soc. A*, 1845 (1969).

17 R. J. Budly and B. J. Hathaway, *J. Chem. Soc. A*, 1725 (1970).

18 L. Scacconi, M. Ciampolini and N. Nardi, *J. Am. Chem. Soc.*, *86*, 819 (1964).

19 G. W. Everett, Jr. and R. H. Holm, *J. Am. Chem. Soc.*, 88, 2442 (1966).

20 L. Carlin in "Transition Metal Chemistry", Marcel Dekker, New York, (1964) Vol. 1, p. 1.

21 a) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, *38*, 683 (1965). b) *Ibid.*, *40*, 1298 and 1854 (1967).

22 L. Sacconi, M. Ciampolini and G. P. Speroni, *J. Am. Chem. Soc.*, *87*, 3102 (1965).

23 L. Sacconi, M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, *4*, 1116 (1965).