

Polynuclear Complexes of Lanthanides with Nickel and Copper Schiff Bases as Ligands

A. SEMINARA, S. GIUFFRIDA, A. MUSUMECI and I. FRAGALÀ

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università, Viale A. Doria 8, 95125-Catania, Italy

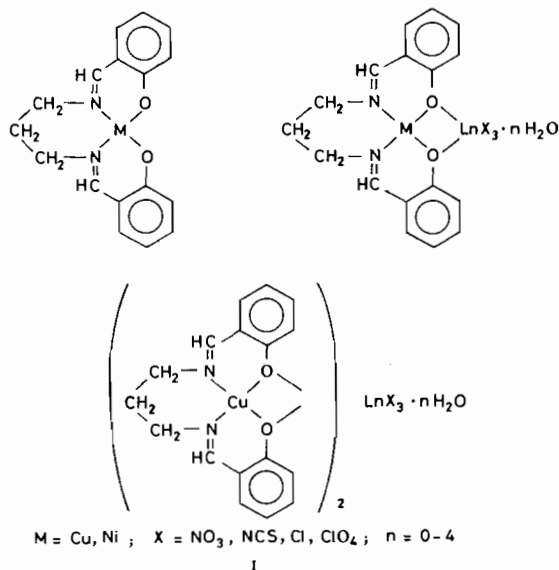
Received January 3, 1984

Polynuclear complexes of lanthanide(III) nitrates, thiocyanates, chlorides and perchlorates with N,N'-1,3-propylen-bis(salicylideneiminato)nickel(II) and N,N'-1,3-propylen-bis(salicylideneiminato)copper(II) have been prepared and characterized by vibrational and electronic spectra, magnetic susceptibility, molar conductivity and thermal analysis measurements. Reliable information relating to the lanthanide-ligand bondings and geometries of the complexes have been inferred from infrared and electronic spectral data.

Introduction

Metal complexes of tetradentate Schiff bases can act as polydentate ligands through the oxygen atoms. This capability has usually been associated with d-transition metal ions [1]. By contrast few data have been reported on the behaviour of lanthanide(III) cations [2, 3].

In this paper we report on the synthesis and properties of polynuclear complexes of N,N'-1,3-propylen-bis(salicylideneiminato)nickel(II) and N,N'-1,3-propylen-bis(salicylideneiminato)copper(II) as ligands with lanthanide(III) nitrates, thiocyanates, chlorides and perchlorates.



Experimental

N,N'-1,3-propylen-bis(salicylideneiminato)nickel(II) (NiPTSB) and N,N'-1,3-propylen-bis(salicylideneiminato)copper(II) (CuPTSB) were prepared following procedures already described [4].

Bi- and trinuclear complexes of lanthanide(III) nitrates, thiocyanates, chlorides and perchlorates with NiPTSB and CuPTSB ligands were obtained by mixing and stirring 1.0 mmol of the appropriate cation in 10 ml of anhydrous ethanol with 2.5 mmoles of the ligand in 20 ml of the same solvent. Microcrystalline products rapidly formed. They were filtered off, washed with anhydrous ethanol and dried under vacuum at room temperature.

Infrared and electronic spectra, molar conductivity, thermal analysis and magnetic susceptibility measurements were carried out following procedures described previously [5, 6].

Results and Discussion

The reaction of NiPTSB and CuPTSB with lanthanide(III) cations leads to formation of microcrystalline products that, on the basis of their elemental and thermal analysis, molar conductivity and infrared spectra can be formulated as $\text{Ln}(\text{L})_n\text{X}_3 \cdot m\text{H}_2\text{O}$, where $\text{L} = \text{NiPTSB, CuPTSB}$; $\text{X} = \text{NO}_3, \text{NCS, Cl, ClO}_4$; $n = 1, 2$; $m = 0-4$. Analytical data, molar conductivity and temperatures of thermal decomposition are collected in Tables I and II. The complexes are moderately soluble in acetonitrile, alcohols and nitromethane and are decomposed by water. Molar conductivity values indicate that the nitrate and thiocyanate complexes are non-electrolytes. Chloride complexes behave in acetonitrile-ethanol mixture (1:1) as 1:1 electrolytes. Values obtained for the perchlorate complexes in acetonitrile are too small to be simply attributed to ion association and suggest contribution of coordinative effects. Molecules of water are present both in the inner and outer coordination spheres of all thiocyanates and of chloride complexes of lighter cations. Dehydration of these complexes in fact occurs through two consecutive endothermic processes between 70 and 160 °C. For

TABLE I. Analytical Data, Electrolytic Conductivity and Temperature of Thermal Decomposition of Lanthanide Bi- and Trinuclear Complexes with NiPTSB (NiPTSB = N,N'-1,3-propylen-bis(salicylideniminato)nickel(II)). In parenthesis the calcd. values.

Compounds	Ln	%N	%Ln	%Ligand ^a	Λ_M^b	Decomp. temp. °C
Ln(NiPTSB) ₂ (NO ₃) ₃ (Ln = La–Sm)	La	9.65(9.77)	13.67(13.85)	67.43(67.60)	19	230
	Nd	9.61(9.72)	14.20(14.30)	67.18(67.25)	21	240
Ln(NiPTSB)(NO ₃) ₃ ·2H ₂ O (Ln = Eu–Lu)	Eu	9.77(9.82)	21.22(21.31)	47.29(47.55)	15	215
	Tb	9.61(9.73)	21.95(22.07)	46.92(47.09)	16	220
	Yb	9.35(9.54)	23.41(23.57)	46.05(46.18)	12	220
Ln(NiPTSB) ₂ (NCS) ₃ ·3H ₂ O (Ln = La–Dy)	La	9.18(9.38)	13.07(13.29)	64.29(64.87)	27	250
	Nd	9.21(9.33)	13.25(13.73)	64.27(64.54)	31	250
	Tb	9.02(9.20)	14.65(14.92)	63.29(63.65)	25	260
Ln(NiPTSB) ₂ (NCS) ₃ ·4H ₂ O (Ln = Ho–Lu)	Ho	8.89(9.00)	15.02(15.14)	62.10(62.25)	28	258
	Tm	8.67(8.97)	15.25(15.45)	61.88(62.02)	18	260
Ln(NiPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O (Ln = La–Lu)	La	4.08(4.33)	10.41(10.73)	52.32(52.41)	225	280 ^c
	Eu	4.11(4.29)	11.39(11.63)	51.67(51.89)	255	290 ^c
	Er	4.00(4.24)	12.23(12.65)	51.07(51.29)	280	290 ^c
Ln(NiPTSB) ₂ Cl ₃ ·4H ₂ O (Ln = La–Sm)	La	5.22(5.63)	13.68(13.95)	67.98(68.12)	75	280
	Nd	5.41(5.60)	14.29(14.41)	67.53(67.76)	70	260
Ln(NiPTSB) ₂ Cl ₃ ·2H ₂ O (Ln = Eu–Lu)	Eu	5.49(5.76)	15.45(15.63)	69.61(69.73)	60	260
	Yb	5.31(5.64)	17.27(17.42)	68.05(68.25)	60	270

^aNiPTSB was detected by gravimetric determination. ^bOhm⁻¹ cm² mole⁻¹; c = 2–4·10⁻³ M; 25 ± 0.1 °C. ^cViolent decomposition.

TABLE II. Analytical Data, Electrolytic Conductivity and Temperature of Thermal Decomposition of Lanthanide Trinuclear Complexes with CuPTSB (CuPTSB = N,N'-1,3-propylen-bis(salicylideniminato)copper(II)). In parentheses the calcd. values.

Compounds	Ln	%N	%Ln	%Ligand ^a	Λ_M^b	Decomp. temp. °C
Ln(CuPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O (Ln = La–Lu)	La	4.15(4.30)	10.31(10.66)	52.35(52.77)	235	285 ^c
	Nd	4.09(4.28)	10.87(11.02)	52.29(52.55)	270	290 ^c
	Gd	4.05(4.24)	11.77(11.90)	51.88(52.03)	265	290 ^c
	Tm	4.01(4.20)	12.48(12.67)	51.39(51.58)	295	300 ^c
Ln(CuPTSB) ₂ (NCS) ₃ ·3H ₂ O (Ln = La–Dy)	La	9.05(9.29)	13.07(13.17)	65.10(65.20)	31	240
	Pr	9.15(9.28)	13.21(13.33)	64.88(65.07)	25	250
	Eu	8.91(9.07)	13.95(14.06)	63.52(63.63)	28	250
Ln(CuPTSB) ₂ (NCS) ₃ ·4H ₂ O (Ln = Ho–Lu)	Ho	8.62(8.92)	13.58(13.83)	62.28(62.58)	20	245
	Yb	8.53(8.86)	15.51(15.63)	62.02(62.13)	30	250

^aCuPTSB was determined by copper volumetric titration. ^bOhm⁻¹ cm² mole⁻¹; c = 2–4·10⁻³ M; 25 ± 0.1 °C. ^cViolent decomposition.

the other chloride and nitrate complexes a single dehydration process occurs between 110 and 160 °C. This behaviour is typical of coordinated water molecules.

IR Spectra

The strong band at 1615 cm⁻¹ in the spectra of both ligands is attributed to overlapping of C=N stretching and aromatic ring modes. Upon complexa-

tion with lanthanide(III) cations this band shifts to higher frequencies and shows three components which peak at 1635, 1620 and 1600 cm⁻¹. The relatively high intensity of the component at 1635 cm⁻¹ is typical of the C=N stretching vibration.

The attribution of the phenolic C–O stretching mode is a debated question. It has been associated with a band at 1540 cm⁻¹ or at 1340 cm⁻¹. Sinn *et al.* [1] suggested the 1540 cm⁻¹ frequency because

TABLE III. Electronic Spectra of Lanthanide(III) Complexes with NiPTSB and CuPTSB (frequency values in kK; in parentheses the extinction coefficient values). f-f bands are not reported.

Complex	Acetonitrile ^a	Solid
NiPTSB	20.41(370); 16.95(64)	20.20; 16.13sh
La(NiPTSB) ₂ (NCS) ₃ ·3H ₂ O	17.86(55); 15.27(24); 12.82(13); 9.52sh; 8.20(49); 7.69sh	17.61; 14.71; 12.99; 9.81sh 8.31* ^b
Nd(NiPTSB) ₂ (NCS) ₃ ·3H ₂ O	17.61(69); 14.71(18); 12.05(11); 10.00sh; 8.33(58); 7.69sh	17.61; 14.50; 12.84; 8.20*; 7.69sh
Ho(NiPTSB) ₂ (NCS) ₃ ·3H ₂ O	17.02(57); 14.28(22); 12.05(9); 9.71sh; 8.13(43); 7.69sh	17.74; 14.25; 12.05; 10.00sh 8.00; 7.69sh
La(NiPTSB) ₂ Cl ₃ ·4H ₂ O	18.18(49); 14.71(18); 12.99(10); 8.33(41)*	17.86; 12.99; 8.00*
Nd(NiPTSB) ₂ Cl ₃ ·2H ₂ O	18.03(47); 14.62(15); 12.99(13); 8.20(38)*	17.74; 12.05; 8.33; 7.14
Er(NiPTSB) ₂ Cl ₃ ·2H ₂ O	17.86(51); 14.62(28); 12.84(14); 9.81sh; 8.00(45)	17.02; 12.84; 10.00sh; 7.94
La(NiPTSB) ₂ (NO ₃) ₃	17.86(52); 14.62(37); 12.84(20); 9.70sh; 8.13(41); 7.69sh	17.86; 13.33; 9.09; 7.69sh
Nd(NiPTSB)(NO ₃) ₃ ·2H ₂ O	17.74(43); 14.71(28); 12.99(9); 9.70sh; 8.00(43)*	17.74; 12.99; 8.33; 7.14sh
Er(NiPTSB)(NO ₃) ₃ ·2H ₂ O	17.74(37); 15.27(21); 12.99(12); 9.50sh; 8.00(44); 7.49sh	17.02; 12.99; 8.13; 7.45sh
Eu(NiPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O	18.18(35); 14.62(19); 12.05(8); 9.09sh; 8.31(28)*	17.70; 14.25; 12.84; 8.00*
Ho(NiPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O	17.70(48); 14.25(27); 12.84(12); 10.00sh; 8.13(41); 7.69sh	17.70; 14.25; 12.50. 8.00*
CuPTSB	16.50(85)	17.05; 15.63sh
La(CuPTSB) ₂ (NCS) ₃ ·3H ₂ O	16.26(56); 9.09(11)	16.50
Nd(CuPTSB) ₂ (NCS) ₃ ·3H ₂ O	16.13(58); 9.25(8)	16.50; 9.25
Ho(CuPTSB) ₂ (NCS) ₃ ·3H ₂ O	16.13(63); 9.25(9)	16.13; 9.25
Nd(CuPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O	16.00(49)	16.26
Ho(CuPTSB) ₂ (ClO ₄) ₃ ·4H ₂ O	16.00(53)	16.26

^aThe chloride complexes in acetonitrile-ethanol mixture (1:1). *Broad. ^bParamagnetic.

of the shift to higher frequencies observed upon complexation as the result of an increased constraint. In the present case, however, the polynucleation of ligand with lanthanide(III) cations causes the composite band centered at 1340 cm⁻¹ to shift drastically to lower frequencies (40–30 cm⁻¹). This result suggests the assignment of the band at 1340 cm⁻¹ to the C–O stretching mode. This assignment, entirely in accord with previous assignments [7, 8], is consistent with the drainage of electron density from the oxygen atoms due to polynucleation.

In the CsBr region the spectra do not show bands up to 250 cm⁻¹ that can be reasonably assigned to Ln–O stretching vibrations.

In the regions of the anion absorptions, the spectra of the complexes with lanthanide(III) nitrates show bands at 1480, 1310, 1035, 812 and 745 cm⁻¹ assigned to the ν_1 , ν_4 , ν_2 , ν_3 and ν_5 modes of coordinated nitrate groups (C_{2v} symmetry). Their bidentate character is indicated by the large splitting (30–40 cm⁻¹) of the combination bands $\nu_2 + \nu_5$ and $\nu_2 + \nu_6$ at 1770 and 1730 cm⁻¹ [9].

The IR spectra of the present perchlorate complexes suggest that both coordinated and uncoordinated perchlorate groups act in the complexes. The spectra show bands at 1150, 1110, 1060 and 935 cm⁻¹ due respectively to the ν_1 , ν_6 , ν_8 and ν_2 vibrations of the perchlorate group having C_{2v} symmetry and strong bands at 1095 and 625 cm⁻¹ due to the ν_3 and ν_4 modes of the perchlorate group having T_d symmetry.

A strong band associated with the C≡N stretching vibration appears in the region up to 2000 cm⁻¹ of the spectra of the lanthanide(III) thiocyanate complexes. This band is largely split into three or four peaks between 2130 and 2050 cm⁻¹ in the spectra of the complexes with NiPTSB (Fig. 1). The splitting probably arises from inequivalence of the three thiocyanate groups because of anion bridging interactions. Bands around 2050 cm⁻¹ are in fact typical of N-coordination while S-coordination is characterized by bands around 2120 cm⁻¹ [10].

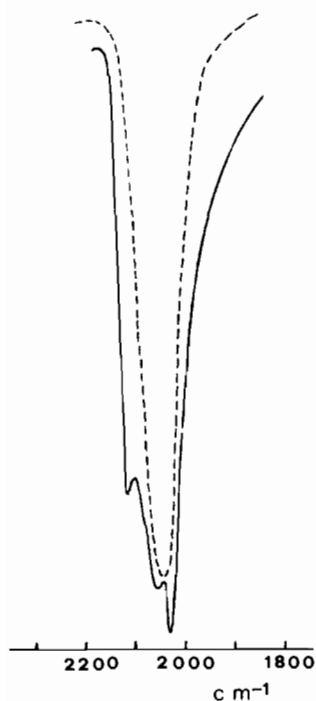


Fig. 1. Infrared spectra in the region of the C≡N stretching vibration: (—) $\text{Nd}(\text{NiPTSB})_2(\text{NCS})_3 \cdot 3\text{H}_2\text{O}$; (---) $\text{Nd}(\text{CuPTSB})_2(\text{NCS})_3 \cdot 3\text{H}_2\text{O}$.

Electronic Spectra

The electronic spectra of NiPTSB and CuPTSB have been previously studied and interpreted in terms of nearly planar environments around the metal ions slightly distorted towards tetrahedral geometries [1, 4].

The lanthanide(III) complexes with CuPTSB are green and indefinitely stable in air. Their reflectance spectra, apart from f-f bands, are comparable one to another and consist of an unique,

though asymmetric band around 16500 cm^{-1} (Table III and Fig. 2). In acetonitrile and nitromethane solutions this band becomes more symmetrical and shifts to lower frequencies. A much weaker band appears in some spectra around 9000 cm^{-1} . These spectra are similar to those reported for the complexes of the same ligand with lanthanide(III) nitrates and described in terms of an increasing distortion of the nearly planar copper(II) environment towards tetrahedral geometry [2]. However, in several cases the exhibition of an unique band of relatively low intensity is consistent with rather symmetrical structures. In consideration both of the well-known tendency of the copper(II) ion to expand its coordination sphere and of the existing ambiguity in the assignment of a certain geometry based only upon electronic data [11], the spectra of the present complexes may also represent apical expansion through cation-solvent or anion bridging interactions towards distorted octahedrons.

Polynuclear complexes of NiPTSB with lanthanides are brown or green-brown in the solid state, but tend to acquire a green colour in acetonitrile and nitromethane solutions.

Apart from f-f bands, the reflectance spectra of the complexes with lanthanide(III) nitrates, chlorides and perchlorates are similar one to another and consist of a relatively strong ligand field band between $19,000$ and $17,000 \text{ cm}^{-1}$. A much weaker and largely asymmetric band lies in the NIR region while additional bands of lower intensity appear between $15,000$ and $12,000 \text{ cm}^{-1}$. The region up to $22,000 \text{ cm}^{-1}$ is, unfortunately, obscured by strong charge-transfer bands. These spectral patterns can be associated with square planar environments with pronounced tetrahedral distortions. In acetonitrile and nitromethane solutions a new weak band appears

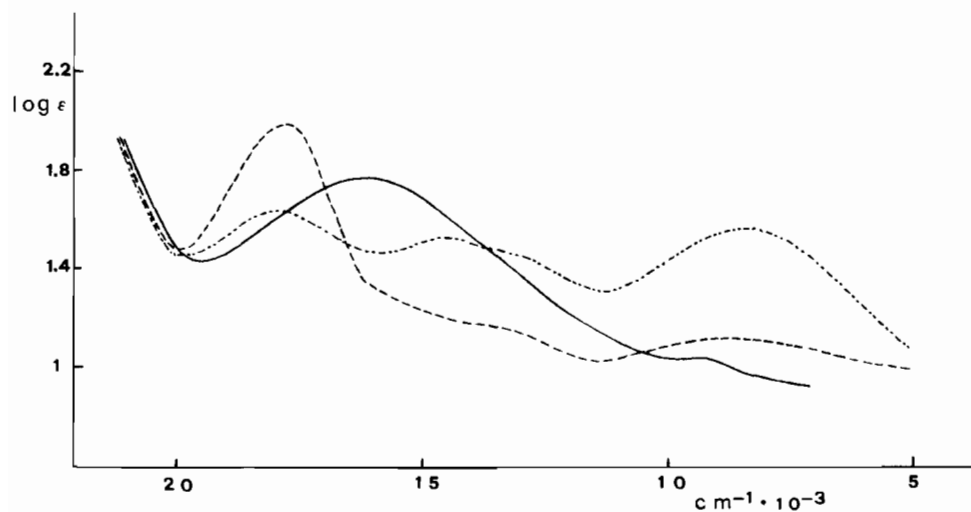


Fig. 2. Electronic spectra: (—) $\text{La}(\text{CuPTSB})_2(\text{NCS})_3 \cdot 3\text{H}_2\text{O}$ in acetonitrile; (---) $\text{La}(\text{NiPTSB})_2(\text{NO}_3)_3$, reflectance spectrum (arbitrary scale of absorbance); (-.-) $\text{La}(\text{NiPTSB})_2(\text{NO}_3)_3$ in acetonitrile.

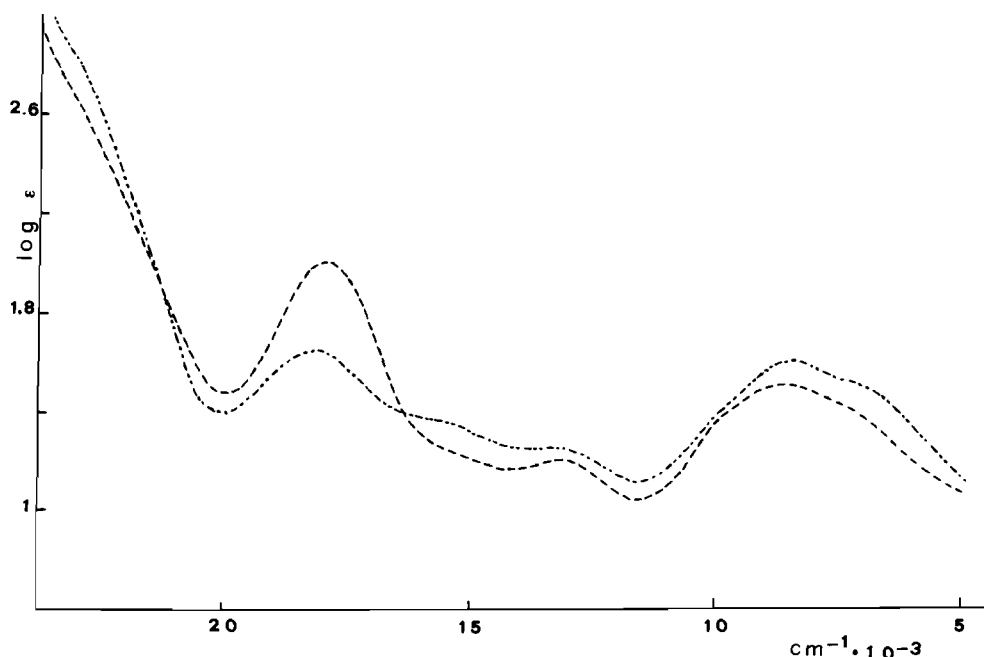


Fig. 3. Electronic spectra: (---) $\text{La}(\text{NiPNTSB})_2(\text{NCS})_3 \cdot 3\text{H}_2\text{O}$, reflectance spectrum (arbitrary scale of absorbance); (-·-·-) $\text{La}(\text{NiPNTSB})_2(\text{NCS})_3 \cdot 3\text{H}_2\text{O}$ in acetonitrile.

at around $15,000\text{ cm}^{-1}$ while the intensity of the bands around $18,000$ and $13,000\text{ cm}^{-1}$ decreases and that of the band around $9,000\text{ cm}^{-1}$ increases (Table III and Fig. 2). These features can be connected with an expansion of the coordination sphere of the nickel(II) ion(s).

The reflectance spectra of NiPNTSB with lanthanide(III) thiocyanates are characterized, in addition to the absorption around $18,000\text{ cm}^{-1}$, by a relatively intense and largely asymmetric band in the NIR region. One or two weak bands appear between $16,000$ and $12,000\text{ cm}^{-1}$. In reality, these spectra resemble those reported for pseudo-tetrahedral nickel(II) complexes [12]. In this case the band appearing in the $15,000$ – $12,000\text{ cm}^{-1}$ region should be assigned to spin-forbidden transition from the free ion 1D state. Tetrahedral structures are, however, scarcely represented when compared with square planar and octahedral structures. Moreover, it is worth noting that polynucleation of this ligand with d-transition metal ions [1] or of similar ligands with lanthanide(III) ions [6] does not affect appreciably the ligation geometry of the adjacent metal ion. It is thus reasonable to interpret these spectra in terms of structures higher than tetraordinated attained, possibly, by anion bridging interactions. The frequencies of the ligand field bands agree with the energy level diagram of high-spin nickel(II) complexes in a square pyramidal structure [13]. The lanthanum(III) complex is paramagnetic; however, since both tetrahedral and square pyramidal (high-spin) structures involve paramagnetism, magnetic susceptibility measurements con-

cerning either the spin-paired or the spin-free lanthanide(III) cations are inconclusive about the geometry of these complexes.

In any case the spectra of the complexes in acetonitrile and nitromethane solutions suggest expansion of the coordination sphere of the nickel(II) ion(s) (Fig. 3).

References

- 1 E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).
- 2 G. Condorelli, I. Fragalà, S. Giuffrida and A. Cassol, *Z. anorg. allg. Chemie*, **412**, 251 (1975).
- 3 G. W. Everett, Jr., D. A. Hanna and J. Y. Lee, *Inorg. Chim. Acta*, **64**, L15 (1981).
- 4 R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).
- 5 A. Seminara, A. Musumeci and A. Chisari, *Inorg. Chim. Acta*, **82**, 173 (1984).
- 6 A. Chisari, A. Musumeci, M. Vidali and A. Seminara, *Inorg. Chim. Acta*, **81**, L19 (1984).
- 7 P. L. Teyessie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963); E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, **26**, 1577 (1964).
- 8 B. Das Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476 (1955).
- 9 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
- 10 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', J. Wiley & Sons, Inc., New York, London (1963).
- 11 E. D. McKenzie, *J. Chem. Soc., A*, 3095 (1970).
- 12 L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).
- 13 M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); *Structure and Bonding*, **6**, Springer-Verlag, Berlin (1969).