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Preparation and Spectroscopic Properties of Oxovanadium(IV) and Dioxomolybdenum(VI) Complexes with Tetraaza[14]annulenes Containing Pyridine Rings

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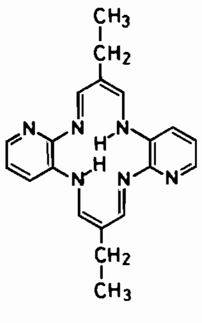
Abstract

The reaction of 5,14-dihydro-7,16-diethyl-(*E*)- or -(*Z*)-dipyrido[b, i][1,4,8,11]tetraazacyclotetradecine with vanadium(III) chloride led to the corresponding oxovanadium(IV) complexes, while reaction with tetracarbonylbis(piperidine)molybdenum(0) gave the corresponding dioxomolybdenum(VI) complexes. The oxovanadium(IV) complexes showed mass spectra with prominent parent peaks in the EI mode. On the other hand the FD mass spectra for the dioxomolybdenum(VI) complexes exhibited the expected parent and parent–O peaks. A V=O stretching band was observed at *ca.* 970 cm^{-1} for the oxovanadium(IV) complexes. The dioxomolybdenum(VI) complexes had strong bands at 855 and 885 cm^{-1} in the NaCl region, which are attributable to the Mo=O symmetric and asymmetric stretching modes. The absorption bands observed above 20 000 cm^{-1} range were attributed to the CT and $\pi \rightarrow \pi^*$ transitions. Judging from the spin Hamiltonian parameters, the oxovanadium(IV) complexes are of square-planar types with an unpaired electron in the d_{xy} orbital. The downfield shifts for the dioxomolybdenum(VI) complexes are much larger in magnitude than those observed for the corresponding oxochromium(IV) complexes. This is primarily dependent on the fact that the magnitude of the positive charge fed by molybdenum(VI) is greater than that by chromium(IV).

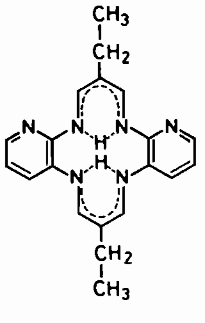
Introduction

Though a lot of papers have been published about transition metal complexes with tetraaza[14]-annulenes [1], relatively little has been presented on their vanadium and molybdenum complexes. A molybdenum carbonyl complex [2] and a dimeric quadruply metal–metal bonded molybdenum(II) complex [3] with a tetraaza[14]annulene were reported previously. However, investigations about synthesis and characterization of oxovanadium(IV) and dioxomolybdenum(VI) complexes with tetraaza[14]annulenes containing pyridine rings have never been reported.

In the present work, we prepared oxovanadium(IV) and dioxomolybdenum(VI) complexes with tetraaza[14]annulene, that is, 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecine (**1-E**) and 5,14-dihydro-7,16-diethyl-(*Z*)-dipyrido[b, i][1,4,8,11]tetraazacyclotetradecine (**1-Z**).



1 - E



1 - Z

This is the first example of a well-characterized dioxomolybdenum(VI) complex with tetraaza[14]-annulenes. We characterized the spectral properties for oxovanadium(IV) and dioxomolybdenum(VI) complexes of the present macrocycles with the aid of mass, vibrational and electronic spectroscopy. The detailed NMR studies for the dioxomolybdenum(VI) complexes and the ESR data for the oxovanadium(IV) complexes are also provided.

Experimental

Physical Measurements

EI mass spectra (at 20 eV) of oxovanadium(IV) complexes and FD mass spectra (at 5.0 kV for cathode and at 25 ~ 30 mA for emitter) of dioxomolybdenum(VI) complexes were performed on a Jeol JMS-DX 300 gas chromatograph–mass spectrometer. Infrared spectra in the range of 400–4000 cm^{-1} were obtained from a KBr technique using a Hitachi 260-10 spectrophotometer at room temperature.

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Electronic spectra covering the 12 500–48 000 cm^{-1} region were carried out with a Shimadzu UV-200S double beam spectrophotometer for methanol solutions at room temperature. ESR spectra were recorded at room temperature on a Jeol JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The oxovanadium(IV) complexes were doped in the isomorphous ligand ($\simeq$1 wt%) and were also run in toluene. The manganese ion diffused into magnesium oxide was employed to obtain standard reference signals for measurements. Proton NMR measurements were taken using a Jeol JNM-FX 60 spectrometer operating in the Fourier transfer mode. The NMR spectra were measured in chloroform-d and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard. Melting points were measured on a Yanaco micro melting point apparatus MP-S3 and uncorrected. Elemental analyses were performed with a Yanaco CHN Corder MT-3.

Preparation of the Macrocycles

5,14-Dihydro-7,16-diethyl-(E)-dipyrido[b,i]-[1,4,8,11]tetraazacyclotetradecine (1-E) and 5,14-dihydro-7,16-diethyl-(Z)-dipyrido[b,i]-[1,4,8,11]tetraazacyclotetradecine (1-Z)

The synthetic procedures for **1-E** and **1-Z** have been reported previously [1t].

Preparation of the Macrocyclic Complexes

(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxovanadium(IV) (VO-(1-E))

A mixture of **1-E** (0.10 g), vanadium(III) chloride (0.50 g) and *N,N*-dimethylformamide (5.0 ml) was heated under reflux for 10 h. To the reaction mixture was added water (100 ml). The precipitates were separated, washed with methanol (5 ml) and extracted with dichloromethane (20 ml). The extract was concentrated to *ca.* 2 ml *in vacuo* and dark green fine needles were obtained; yield 0.02 g (17%), melting point >300 °C. The mass spectrum showed M^+ at m/z 411 and peaks for $[M-CH_3]^+$ and $[M-2CH_3]^+$ at m/z 396 and 381, respectively. IR (KBr disk): 1595 (C=C str. (conjugated ring)), 1563 (C=N str.), 1418 (macrocyclic skeletal str.) and 968 (V=O str.) cm^{-1}.

(7,16-Diethyl-(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxovanadium(IV) (VO(1-Z))

The reaction of **1-Z** (0.10 g) and vanadium(III) chloride in *N,N*-dimethylformamide (5 ml), following the above procedure, gave dark green fine needles; yield 0.03 g (25%), melting point >300 °C. The mass spectrum showed M^+ at m/z 411 and peaks for $[M-CH_3]^+$ and $[M-2CH_3]^+$ at m/z 396 and 381, respectively. IR (KBr disk): 1590 (C=C str. (conjugated ring)), 1560 (C=N str.), 1423 (macrocyclic skeletal str.) and 975 (V=O str.) cm^{-1}.

*(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)dioxomolybdenum(VI) (**MoO$_2$-(1-E)**)*

A mixture of **1-E** (0.20 g), tetracarbonylbis(piperidine)molybdenum(0) (0.40 g) [4], cyclohexanol (1 ml) and *N,N*-dimethylformamide (14 ml) was heated under reflux in argon atmosphere with stirring for 8 h. Solvents were removed under reduced pressure. The solid residue was washed with hexane (10 ml). The dichloromethane solution of the residue was applied on the top of a chromatographic column of activated aluminium oxide (200 mesh, Wako Pure Chemical Industries, Ltd.). A deeply colored band on the top of the column was eluted with dichloromethane, and then with chloroform. The second deep red effluent (chloroform as eluant) was collected and evaporated to dryness *in vacuo*. The solid residue was recrystallized from dichloromethane–hexane to give vermilion fine needles; yield 0.06 g (22%), melting point >300 °C. The mass spectrum showed M^+ at m/z 474 and peaks for $[M-O]^+$ and $[M-2O]^+$ at m/z 458 and 442, respectively. IR (KBr disk): 1592 (C=C str. (conjugated ring)), 1560 (C=N str.), 1403 (macrocyclic skeletal str.), 885 (Mo=O str.) and 855 (Mo=O str.) cm^{-1}.

*(7,16-Diethyl-(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)dioxomolybdenum(VI) (**MoO$_2$-(1-Z)**)*

This reaction of **1-Z** (0.20 g) and tetracarbonylbis(piperidine)molybdenum(0) (0.60 g) in a mixed solvent composed of *N,N*-dimethylformamide (14 ml) and cyclohexanol (3 ml), following the above procedure, gave vermilion fine needles; yiels 0.07 g (26%), melting point >300 °C. The mass spectrum showed M^+ at m/z 474 and peaks for $[M-O]^+$ and $[M-2O]^+$ at m/z 458 and 442, respectively. IR (KBr disk): 1595 (C=C str. (conjugated ring)), 1565 (C=N str.), 1402 (macrocyclic skeletal str.), 885 (Mo=O str.) and 855 (Mo=O str.) cm^{-1}.

Results and Discussion

Synthesis of the Macrocyclic Complexes

The reaction of **1-E** or **1-Z** with vanadium(III) chloride in refluxing *N,N*-dimethylformamide for 10 h gave the oxovanadium(IV) complexes, **VO(1-E)** and **VO(1-Z)**, in 17 and 25% yields, respectively. The corresponding reaction of tetracarbonylbis(piperidine)molybdenum(0) with **1-E** or **1-Z** occurred within 8 h in the blended solvent of *N,N*-dimethylformamide and cyclohexanol at reflux temperature to give the dioxomolybdenum(VI) complexes, **MoO$_2$-**

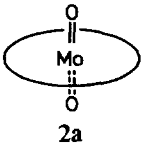
TABLE 1. Analytical Data for Macrocyclic Complexes

Compound		Found (%)			Calculated (%)		
		C	H	N	C	H	N
$C_{20}H_{20}N_6OV$	VO(1-E)	58.40	5.07	20.02	58.40	4.90	20.43
$C_{20}H_{20}N_6OV$	VO(1-Z)	58.24	4.92	20.40	58.40	4.90	20.43
$C_{20}H_{20}N_6O_2Mo$	MoO_2(1-E)	51.09	4.29	18.10	50.86	4.27	17.79
$C_{20}H_{20}N_6O_2Mo$	MoO_2(1-Z)	50.54	4.21	17.80	50.86	4.27	17.79

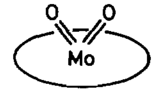
(1-E) and MoO_2(1-Z) in 22 and 26% yields each. The analytical data for the macrocyclic complexes are collected in Table 1. Elemental analyses of crystalline samples of **VO(1-E)**, **VO(1-Z)**, **MoO_2(1-E)** and **MoO_2(1-Z)** were consistent with compounds for the formula macrocyclic oxovanadium(IV) and dioxomolybdenum(VI) complexes, respectively. The two vanadium complexes gave mass spectra with the molecular ion peak at mass number 411, which was assigned to originate from $[VO(1\text{-}E)]^+$ or $[VO(1\text{-}Z)]^+$. On the other hand the mass spectra of the molybdenum complexes in FD mode and at 30 °C exhibited the expected molecular ion peak, $[MoO_2(1\text{-}E)]^+$ or $[MoO_2(1\text{-}Z)]^+$ (m/z 474, ^{98}Mo). At higher temperatures and in EI mode, only m/z 458 was observed, which is consistent with $[MoO(1\text{-}E)]^+$ or $[MoO(1\text{-}Z)]^+$; a good fit was obtained between the calculated and observed isotopic distributions.

Vibrational Spectra

The infrared spectra of **VO(1-E)**, **VO(1-Z)**, **MoO_2(1-E)** and **MoO_2(1-Z)** are shown in Fig. 1 for the region of 800–1000 cm^{-1}. As described in porphyrin and related oxovanadium complexes previously [5–7], the V=O stretching mode causes a strong absorption band in the range of 950–1000 cm^{-1}. Therefore, the absorption band at around 970 cm^{-1} for the present vanadium complexes is attributed to the V=O stretching mode. The molybdenum complexes, MoO_2(1-E) and MoO_2(1-Z), show two strong absorption bands due to the MoO_2 group in the range from 850 to 900 cm^{-1} as shown in Fig. 1. According to the criterion proposed previously [7–13], it may be presumed that the two oxygen atoms of the molybdenyl group are *cis* to each other in the present complexes as in **2b** and the two bands may be attributable to the symmetric and asymmetric stretching modes of the *cis*-dioxo group, respectively.



2a



2b

Electronic Spectra

The electronic absorption spectra for **VO(1-E)** and **MoO_2(1-E)** as an example are shown in Fig. 2, covering the 15000–45000 cm^{-1} range. The spectral features for **VO(1-E)** and **VO(1-Z)**, and **MoO_2(1-E)**

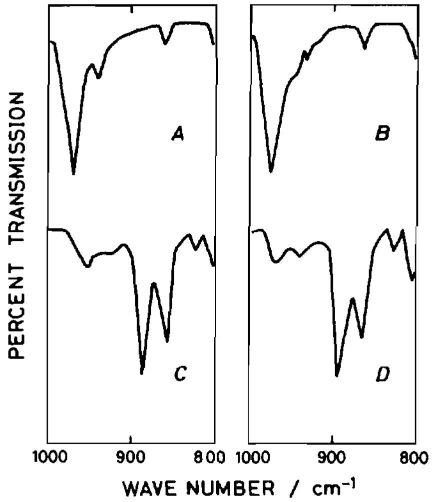


Fig. 1. Infrared spectra of macrocyclic oxovanadium(IV) and dioxomolybdenum(VI) complexes by a KBr method. A, VO(1-E); B, VO(1-Z); C, MoO_2(1-E); D, MoO_2(1-Z).

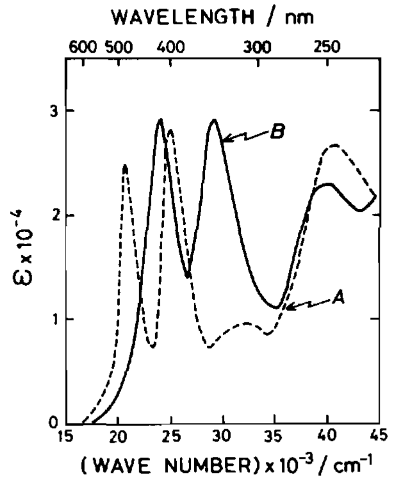


Fig. 2. Electronic spectra of 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecine complexes in methanol at room temperature. A, VO(1-E); B, MoO_2(1-E).

and MoO_2(**1-Z**) respectively, are analogous to one another. The absorption bands appearing in the energy region greater than 20 000 cm^{-1} are attributable to charge-transfer transitions from metal to ligand and $\pi \rightarrow \pi^*$ transitions within a ligand molecule, and not of $d \rightarrow d^*$ origin, because the molar extinction coefficients of these bands are much larger than those commonly assigned to $d \rightarrow d^*$ transitions [14, 15].

ESR Spectra

The spin Hamiltonian parameters for the present macrocyclic oxovanadium(IV) complexes are compiled in Table 2. The ESR spectrum recorded at room temperature for a $10^{-2} \sim 10^{-3}$ mol dm^{-3} solution of **VO(1-E)** or **VO(1-Z)** in toluene consists of a set of eight hyperfine lines and, as expected, the magnetic interaction between the unpaired electron and the vanadium nucleus ($I = 7/2$) is evident. The general features of the spectra for **VO(1-E)** and **VO(1-Z)** are similar to each other and to that observed for the (5,10,15,20-tetraphenylporphinato)oxovanadium(IV) complex [16]. The ESR spectrum of the (7,16-diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxovanadium(IV) complex magnetically diluted in the corresponding metal-free ligand to a ratio of 1:100 at room temperature is shown in Fig. 3 as an example. The spectral features of **VO(1-E)** and **VO(1-Z)** are also similar to one another. The spectrum is made up of two sets of eight vanadium hyperfine lines that correspond to $g_\parallel$ and $g_\perp$ components. The two weak peaks at low-field and the three highest-field peaks correspond to the $g_\parallel$ component while the central strong peaks are associated with the $g_\perp$ component. A similar spectrum was also observed for the oxovanadium(IV) complexes derived from porphyrin [16] and phthalocyanine [6, 17, 18]. In this spectrum, we did not detect any extra hyperfine structure due to magnetic interaction between an unpaired electron in vanadium(IV) and nitrogen nuclei ($I = 1$). Accordingly, the present oxovanadium(IV) complexes assume a square-planar type with an unpaired electron in the d_{xy} orbital such as those of porphyrin and phthalocyanine.

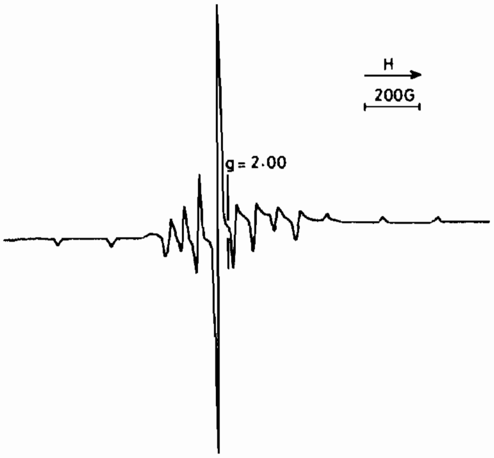


Fig. 3. ESR spectrum of (7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxovanadium(IV) complex magnetically diluted in the corresponding metal-free ligand at room temperature.

NMR Spectra

Consistent with a diamagnetism of the present macrocyclic dioxomolybdenum complexes, **MoO_2(1-E)** and **MoO_2(1-Z)** gave well-resolved proton NMR spectra. Chemical shift assignments were made on the basis of comparisons with the metal-free ligands [1t] and their nickel(II) and oxochromium(IV) complexes [1w]. Proton NMR data and their assignments for **MoO_2(1-E)** and **MoO_2(1-Z)** are summarized in Table 3. The methine H_a-proton signal obtained in the lowest field is shifted downfield by 1.73–1.93 ppm and the methine H_b-proton peak is also shifted downfield by 1.58–1.65 ppm on formation of the dioxomolybdenum complexes. The magnitude of the downfield shifts is much larger than that observed for the nickel(II) and the oxochromium(IV) complexes [1w]. This downfield shift can be attributed to the deshielding effect due to the positive charge provided by the metal ion in the complexes. Since the oxidation number of the molybdenum is greater than that of the nickel and the chromium, the deshielding effect for the dioxomolybdenum(VI) complexes is much greater than that of the nickel(II) and the oxo-

TABLE 2. Spin Hamiltonian Parameters for the Oxovanadium(IV) Complexes[a,b]

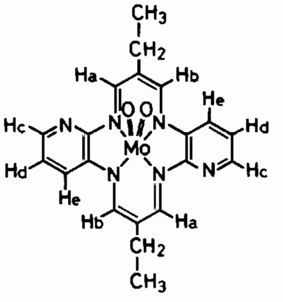
Complex	Medium	$\bar{g}$	$g_\parallel$	$g_\perp$	$\bar{A}^V \times 10^4$ (cm^{-1})	$A_\parallel^V \times 10^4$ (cm^{-1})	$A_\perp^V \times 10^4$ (cm^{-1})
VO(1-E)	toluene[c]	1.995			86.6		
	ligand		1.963	1.996		151.8	55.0
VO(1-Z)	toluene[c]	1.994			86.6		
	ligand		1.962	1.997		151.9	54.8

[a] Measured at room temperature. [b] Maximum possible errors: g, ±0.0005; $\bar{A}^V, A_\parallel^V, A_\perp^V$, $\pm 0.5 \times 10^{-4}$ cm^{-1}. [c] Concentration of the oxovanadium(IV) complex, $10^{-2} \sim 10^{-3}$ mol dm^{-3}.

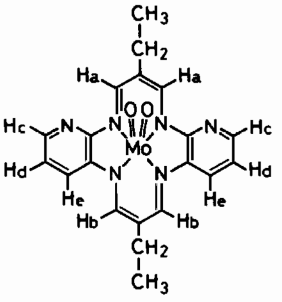
TABLE 3. ^{1}H NMR Data for the Macrocyclic Dioxomolybdenum(VI) Complexes^a

Complex	Ethyl		Aromatic			Methine	
	$-CH_3$	$-CH_2-$	$-H_c$	$-H_d$	$-H_e$	$-H_a$	$-H_b$
MoO_2(1-E)	1.52(t) (J = 7.5 Hz)	3.16(q) (J = 7.5 Hz)	8.34(dd) (J = 5.0 Hz) (J = 1.3 Hz)	7.22(dd) (J = 7.9 Hz) (J = 5.0 Hz)	8.08(dd) (J = 7.9 Hz) (J = 1.3 Hz)	10.06(s)	9.24(s)
MoO_2(1-Z)	1.51(t) (J = 7.5 Hz) 1.54(t) (J = 7.5 Hz)	3.13(q) (J = 7.5 Hz) 3.21(q) (J = 7.5 Hz)	8.35(dd) (J = 4.6 Hz) (J = 1.5 Hz)	7.25(dd) (J = 8.3 Hz) (J = 4.6 Hz)	8.09(dd) (J = 8.3 Hz) (J = 1.5 Hz)	10.11(s)	9.22(s)

^{a}Chemical shifts are given in ppm for TMS as an internal reference. Measured in chloroform-d. Multiplicity of a proton signal is given in parentheses after δ values: s = singlet; t = triplet; q = quartet; dd = doublet of doublets.



MoO_2(1-E)



MoO_2(1-Z)

chromium(IV) complexes. Accordingly the large downfield shift for the dioxomolybdenum complexes is explained on the basis of above deshielding effect. The signals for the aromatic H_c-, H_d- and H_e-protons are shifted downfield by 0.47–0.84 ppm and the signals for the methyl and methylene protons of the 7- and 16-ethyl groups are also shifted downfield by 0.38–0.96 ppm upon dioxomolybdenum(VI) complex formation. Being also larger than that observed for the nickel(II) and the oxochromium(IV) complexes, the magnitude of the downfield shifts for the aromatic, methyl and methylene protons is much smaller than that obtained for the methine protons. This is mainly attributed to the fact that the aromatic, methyl and methylene proton groups are placed further from the positive charge of the molybdenum(VI) ion which affords the deshielding effect.

References

1 (a) H. Hiller, P. Dimroth and H. Pfitzner, *Liebigs Ann. Chem., 717* (1968) 137; (b) E.-G. Jaeger, *Z. Anorg. Allg. Chem., 364* (1969) 177; (c) V. L. Goedken, J. Molim-Case and Y.-A. Whang, *J. Chem. Soc., Chem. Commun.*, (1973) 337; (d) F. A. L'Eplattenier and A. Pugin, *Helv. Chim. Acta, 58* (1975) 917; (e) V. L. Goedken and V.-A. Park, *J. Chem. Soc., Chem. Commun.*, (1975) 214; (f) M. C. Weiss, B. Bursten, S. Peng and V. L. Goedken, *J. Am. Chem. Soc., 98* (1976) 8021; (g) D. R. Neves and J. C. Dabrowiak, *Inorg. Chem., 15* (1976) 129; (h) M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem., 16* (1977) 305; (i) A. Pezeshk, F. T. Greenaway and G. Vincow, *Inorg. Chem., 17* (1978) 3421; (j) Y. Nishida, A. Sumita, K. Hayashida, H. Ohshima, S. Kida and Y. Maeda, *J. Coord. Chem., 9* (1979) 161; (k) P. W. DeHaven and V. L. Goedken, *Inorg. Chem., 18* (1979) 827; (m) J. C. Dabrowiak, D. P. Fisher, F. C. McElroy and D. J. Macero, *Inorg. Chem., 18* (1979) 2304; (n) K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Jpn., 53* (1980) 2262; (o) V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, (1982) 142; (p) K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta, 83* (1984) L67; (q) V. L. Goedken, H. Ito and T. Ito, *J. Chem. Soc., Chem. Commun.*, (1984) 1453; (r) K. Sakata, M. Hashimoto and T. Naganawa, *Inorg. Chim. Acta, 98* (1985) L11; (s) K. Sakata, M. Hashimoto and H. Yoshino, *Inorg. Chim. Acta, 99* (1985) 231; (t) K. Sakata, Y. Hayashida, M. Hashimoto, K. Terada and K. Kato, *Inorg. Chim. Acta, 105* (1985) L25; (u) A. R. Cutler, C. S. Alleyne and D. Dolphin, *Inorg. Chem., 24* (1985) 2276; (v) S. Ciurli, E. M. Meyer, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, (1987) 281; (w) K. Sakata, Y. Hayashida, S. Yanagida, M. Hashimoto and Y. Kato, *Inorg. Chim. Acta, 134* (1987) 269; (x) K. Sakata, T. Naganawa, M. Hashimoto, H. I. Ogawa and Y. Kato, *Inorg. Chim. Acta, 143* (1988) 251; (y) E. Sister, V. Gottfried, M. Kapon, M. Kaftory, Z. Dori and H. B. Gray, *Inorg. Chem., 27* (1988) 600; (z) K. Sakata, T. Kikutake, Y. Shigaki, M. Hashimoto, H. I. Ogawa and Y. Kato, *Inorg. Chim. Acta, 144* (1988) 1.

2 L. G. Bell and J. C. Dabrowiak, *J. Chem. Soc., Chem. Commun.*, (1975) 512.

3 D. Mandon, J.-M. Giraudon, L. Toupet, J. Sala-Pala and J. E. Guerchais, *J. Am. Chem. Soc., 109* (1987) 3490.

4 D. J. Darensbourg and R. L. Kump, *Inorg. Chem., 17* (1978) 2680.

5 J. G. Erdman, V. G. Ramsey, N. W. Kalenda and W. H. Hanson, *J. Am. Chem. Soc., 78* (1956) 5844.

6 J. M. Assour, J. Goldmacher and S. E. Harrison, *J. Chem. Phys., 43* (1965) 159.

7 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd edn., 1978, p. 249.

8 P. C. H. Mitchell, *Quart. Rev., 20* (1966) 103.

9 W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A* (1968) 400.

10 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 9* (1974) 83.

11 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 9* (1974) 161.

12 J. R. Dilworth, C. A. McAuliffe and B. J. Sayle, *J. Chem. Soc.*, Dalton Trans., (1977) 849.
13 H. Ledon and M. Bonnet, *J. Chem. Soc., Chem. Commun.*, (1979) 702.
14 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., 1984.
15 B. N. Figgis, *Introduction to Ligand Fields*, Wiley, New York, 1966.
16 J. M. Assour, *J. Chem. Phys.*, *43* (1965) 2477.
17 E. M. Roberts and W. S. Koski, *J. Chem. Phys.*, *34* (1961) 591.
18 D. Kivelson and S.-K. Lee, *J. Chem. Phys.*, *41* (1964) 1896.