Inorganica Chimica Acta, 39 (1980) 81–90
©Elsevier Sequoia S.A., Lausannne – Printed in Switzerland

Single Crystal Electronic Spectra, Electron Spin Resonance and Magnetic Data for Some High Spin Tetragonal Cobalt(II) Complexes at Cryogenic Temperatures

A. B. P. LEVER, I. M. WALKER
Dept. of Chemistry, York University, Downsview (Toronto), Ont., Canada, M3J 1P3

and P. J. McCARTHY
Dept. of Chemistry, Canisius College, Buffalo, N.Y., 14208, U.S.A.

Received July 3, 1979

The electronic and esr spectra of a series of high spin cobalt(II) complexes of formula $Co(EtNHCH_2CH_2NHEt)_2Z_2$ *(Z = Cl, Tr, NCS,* NO_3*) and* $Co(MeNHCH_2CH_2NHMe)_2(NO_3)_2$ *have been examined at R.T. and 10 K respectively. The single crystal polarised electronic spectra were analysed in terms of the Normalised Spherical Harmonic Hamiltonian and a good fit between observed and calculated band energies was obtained. All the complexes are* trans, *with the exception of* $Co(EtNHCH_2CH_2NHEt)_2(NO_3)_2$ *which is* cis. *The data are consistent with the presence of a* ^4E_g *ground term derived from the cubic* $^4T_{1g}$ *term under the influence of a tetragonal distortion for all but one of the complexes. Orbital angular overlap model parameters were derived for this series. These were compared with similar data for cobalt(II) and nickel(II) in the literature, with special reference to the corresponding nickel(II) ethylenediamine complexes. The chief difference between the cobalt and nickel complexes, in an analogous pair of ethylenediamine complexes, is a significantly larger axial repulsion energy in the nickel case. This is attributed to the presence of an extra anti-bonding electron in nickel(II)* versus *cobalt(II). The esr and magnetic data are fully consistent with the tetragonal model developed for these complexes but do not provide any additional characterisation.*

Introduction

Whilst there have been a multitude of publications concerning the electronic structure of tetragonal

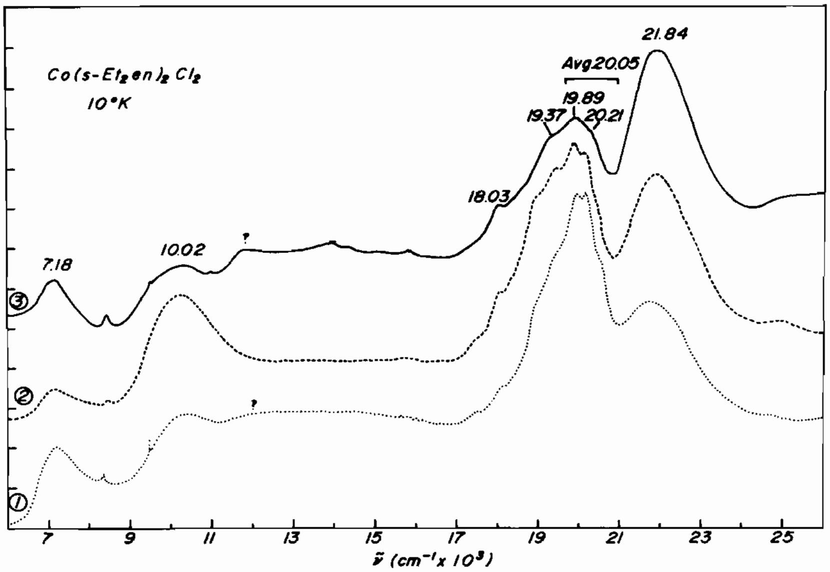

Fig. 1. The single crystal spectra of $Co(s\text{-}Et_2en)_2Cl_2$ at 10 K. The various spectra are recorded along different orthogonal extinction axes. Their relationship to the molecular axes is unknown. The energies of principal band maxima (in kK) are cited. The query sign indicates a band which may be an instrumental artifact. It occurs at a detector changeover.

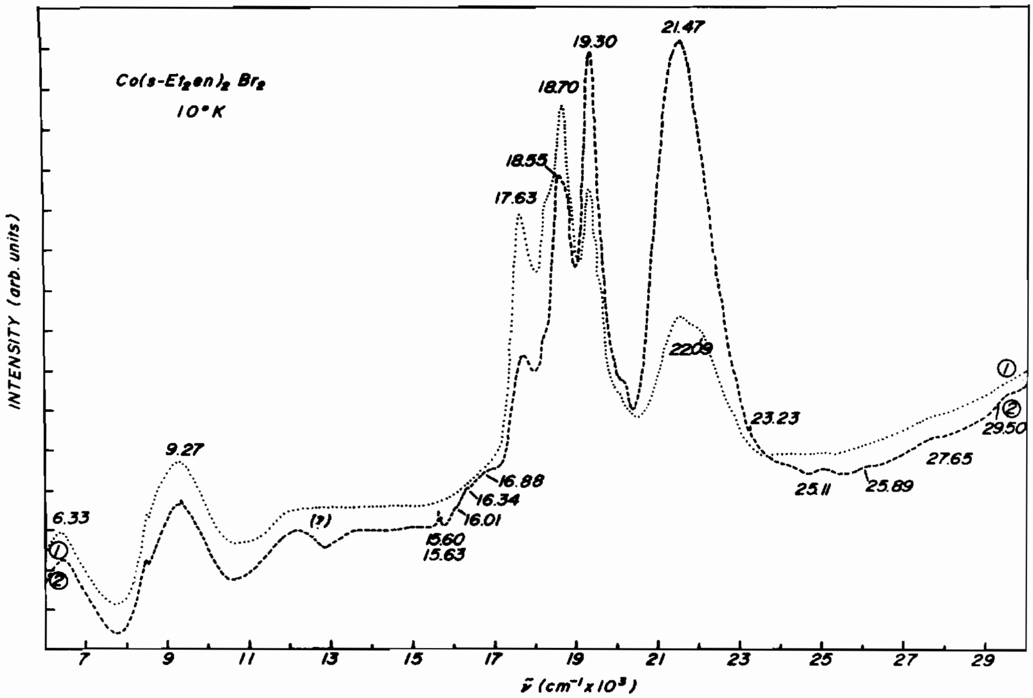

Fig. 2. The single crystal spectra of Co(s-Et_2en)$_2$$Br_2$ at 10 K. For details see legend to Fig. 1.

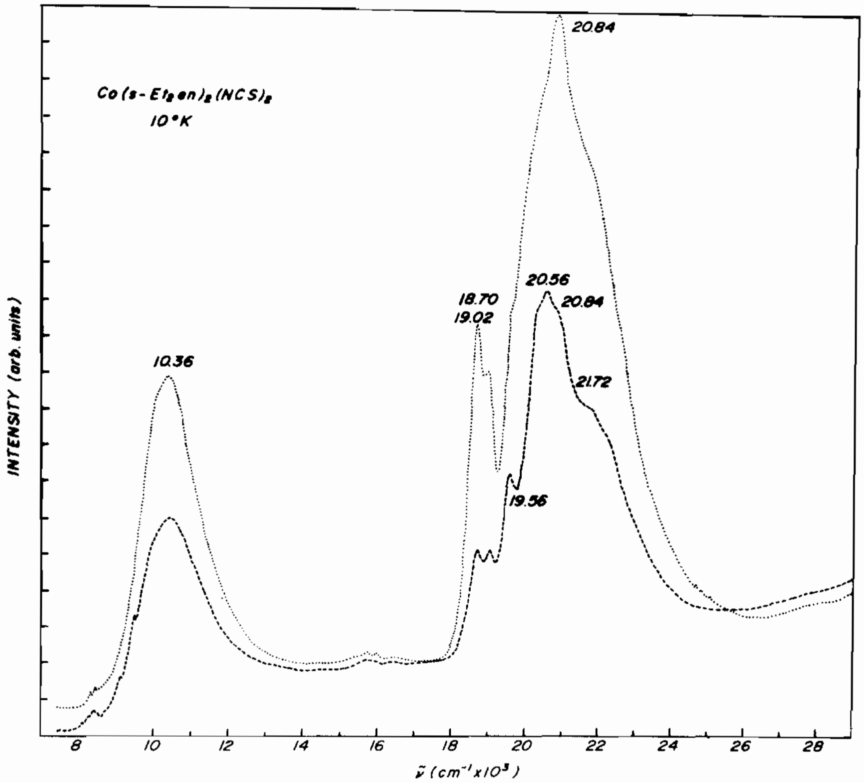

Fig. 3. The single crystal spectra of Co(s-Et_2en)$_2$(NCS)$_2$ at 10 K.

nickel(II) complexes (1, and references therein) few data for tetragonal cobalt(II) have been discussed [2–10]. This is not surprising since in the cobalt series there is ambiguity concerning the ground state, and assignment of the split components of excited states is a more difficult problem because of the possible presence of relatively strong quartet–doublet transitions and possible spin–orbit or vibronic

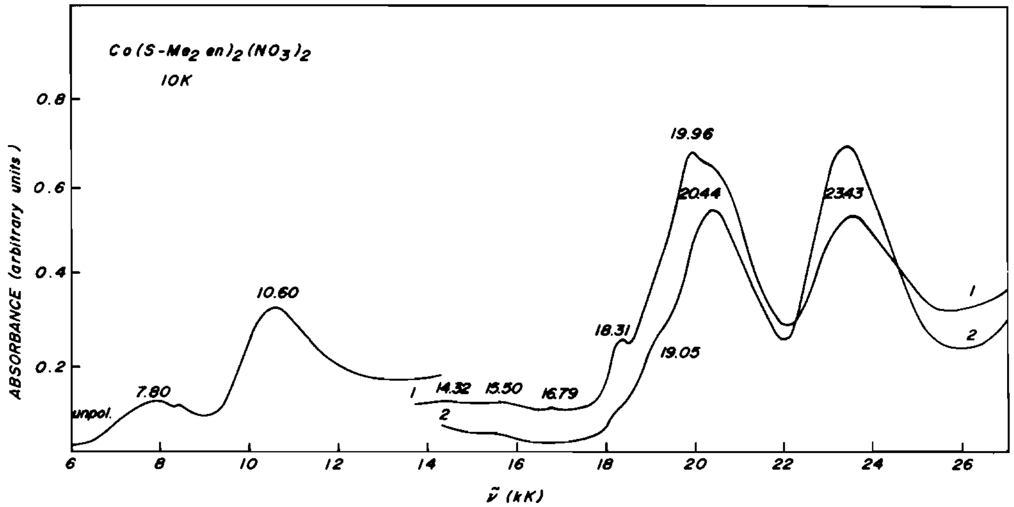

Fig. 4. The single crystal spectra of $Co(s\text{-}Me_2en)_2(NO_3)_2$ at 10 K.

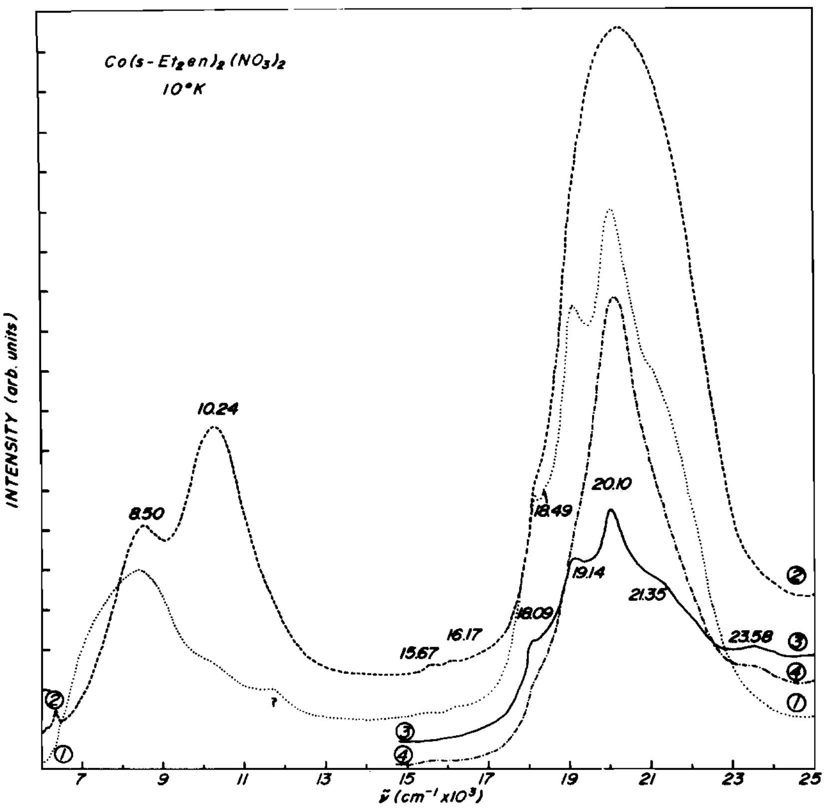

Fig. 5. The single crystal spectra of *cis*-$Co(s\text{-}Et_2en)_2(NO_3)_2$ at 10 K. Spectra (3) and (4) were obtained with a thinner crystal.

contributions [11]. The complexes *trans*-Co(N,N′-R_2-ethylenediamine)$_2Z_2$ (R = Me, Et, Z = Cl, Br, NCS, NO_3) have fingerprint infrared spectra essentially identical with those of their nickel analogs [12], and the two series are certainly isostructural. Co(N,N′-diethylethylenediamine)$_2(NO_3)_2$ has a *cis* configuration (see below) whilst all the remaining complexes are *trans*. Polarised single crystal electronic spectra at 10 K are shown in Figs. 1–5 and the calculated and observed energies are shown in Table I. Unfortunately X-ray data are not available for this series. Although the dichroism data cannot be unequivocally assigned, nevertheless it is possible to arrive at fairly unambiguous assignments. We refer the reader to an earlier discussion [1] of the value of single crystal data when X-ray information is

TABLE I. Comparison of Calculated and Observed (10 K)[a] Spin Allowed Transitions in Co(s-R_2-en)$_2Z_2$ (kK).

		$^4A_{2g}$	$^4B_{2g}$	^4E_g	$^4B_{1g}$	^4E_g	$^4A_{2g}$
Co(s-Et_2en)$_2Cl_2$	obs.	–	7.18	10.02	19.37	20.05	21.84
	calc.	0.582	7.172	10.013	19.368	20.049	21.845
Co(s-Et_2en)$_2Br_2$	obs.	–	6.325	9.27	17.63	19.00	21.47
	calc.	0.331	6.293	9.065	17.593	19.094	21.405
Co(s-Et_2en)$_2$(NCS)$_2$	obs.	–	10.355	10.355	21.72	20.84	20.56
	calc.	0.223	10.365	10.248	21.726	20.977	20.363
Co(s-Et_2en)$_2$(NO_3)$_2$	obs	–	10.24	8.50	19.14	20.10	18.09
	calc.	0.113	10.222	8.308	19.119	20.232	17.937
Co(s-Me_2en)$_2$(NO_3)$_2$	obs.	–	7.80	10.60	19.96	20.435	23.425
	calc.	0.261*	7.707	10.00	19.867	20.488	23.600

[a] The parameter values used are reported in Table II. Co(s-Et_2en)$_2$(NO_3)$_2$ is *cis*, the other complexes are all *trans*. The g subscripts should be dropped from the symmetry labels for the *cis* complex. The ground state is ^4E_g for all the complexes except for Co(s-Me_2en)$_2$(NO_3)$_2$ when it is $^4A_{2g}$. The main features in the room temperature spectra appear at: Co(s-Et_2en)$_2Cl_2$, 7.06; 9.52; 19.06; 19.80; 21.03; 27.18. Co(s-Et_2en)$_2Br_2$, 8.7; 17.36; 18.29; 19.09; 20.97. Co(s-Et_2en)$_2$(NO_3)$_2$, 7.86; 9.90; 18.04sh; 18.84sh; 19.87; 21.32sh; 23.49sh. Co(s-Et_2en)$_2$(NCS)$_2$, 9.81; 18.58; 20.27. Co(s-Me_2en)$_2$(NO_3)$_2$, 7.27; 9.94; 17.85sh; 19.30sh; 20.12; 22.86. *Transition $^4E_g \leftarrow {}^4A_{2g}$.

unavailable. Electron spin resonance data at liquid helium temperature, and magnetic data are also reported here for these species.

Experimental

The ligands $MeNHCH_2CH_2NHMe$ (s-Me_2en) and $EtNHCH_2CH_2NHEt$ (s-Et_2en) were purchased from Koch-Light (UK) or Aldrich (USA) and stored over sodium hydroxide pellets. The complexes were prepared by the literature method [12] and recrystallised slowly from ethanol under a nitrogen blanket. Metal analyses (atomic absorption using a Varian Techtron model 1200) confirmed their purity. The electronic spectra were recorded on a Cary 14 spectrophotometer using procedures previously described [1]. For most of the crystals there was some uncertainty about the baseline in the 11–14 kK region. An absorption band which appears around 12 kK in three of the samples may be spurious. This is noted on the spectra with query marks. Such a feature did not appear in the thiocyanate spectra, perhaps because the crystals of this compound were larger and of finer quality. It should be noted, however, that in the chloro-, bromo- and *trans*-nitrato complexes, quartet–doublet transitions are calculated to appear at 11.89, 11.77 and 12.70 kK resp. (assuming C = 4B) whilst in the thiocyanato complex the quartet–doublet transition closest to 12 kK is calculated to appear at 14.32 kK.

The total band areas at room temperature and 10 K between approximately 14–31 kK were measured for one polarisation of each of the five crystals. The band areas at 10 K for the chloro, bromo, thiocyanato and *trans*-nitrato complexes are 50, 53, 59 and 68% of their room temperature values. This indicates that a principal intensity gaining mechanism is vibronic. If the hyperbolic cotangent law holds, the activating vibrations for these bands would have an energy of about 250 cm^{-1}. The bands of the *cis*-Co(s-Et_2en)$_2$(NO_3)$_2$ complex show little, if any, shrinkage on cooling the sample. Presumably the lower symmetry of the complex permits some static asymmetrical ligand field to be the principal factor which provides intensity to otherwise forbidden transitions. A temperature of 10 K was achieved with an Air Products Displex cryogenic refrigerator. Magnetic data were obtained by the Faraday method using a fully automated Faraday system, previously described [13].

Magnetic Data

Temp. K, χ_M [$\times 10^6$ cgs], μ_{eff} [B.M.] Co(s-Et_2-en)$_2Br_2$ (diamagnetic correction = 257 $\times$ 10^{-6} cgs). 80.2, 32571, 4.57; 98.3, 28465, 4.73; 115.2, 24991, 4.80; 131.8, 22254, 4.84; 148.4, 20044, 4.88; 166.6, 18185, 4.923; 184.0, 16642, 4.95; 201.6, 15309, 4.97; 219.1, 14293, 5.01; 236.4, 13312, 5.02; 254.6, 12436, 5.03; 272.8, 11701, 5.05; 291.0, 11000, 5.06; 309.6, 10475, 5.09; 327.5, 9810, 5.07; Co(s-Et_2en)$_2Cl_2$ (diamagnetic correction = 208 $\times$ 10^{-6} cgs): 79.8, 32099, 4.53; 81.1, 32751, 4.61; 99.76, 28063, 4.73; 117.1, 24412, 4.78; 134.2, 21631, 4.82; 151.9, 19374, 4.85; 169.8, 17522, 4.88; 188.0, 15961, 4.90; 205.8, 14806, 4.94; 224.1, 13650, 4.95; 242.5, 12727, 4.97; 260.4, 11860, 4.97; 279.6, 11110, 4.985; 297.8, 10476, 5.00; 316.7, 9900, 5.01. Co(s-Et_2en)$_2$(NCS)$_2$ (diamagnetic correction = 250 $\times$ 10^{-6} cgs): 79.7, 32456, 4.55; 98.2, 28370, 4.72; 114.9, 24931, 4.79; 131.35, 22241, 4.835; 147.9, 19994, 4.86; 166.0, 18122,

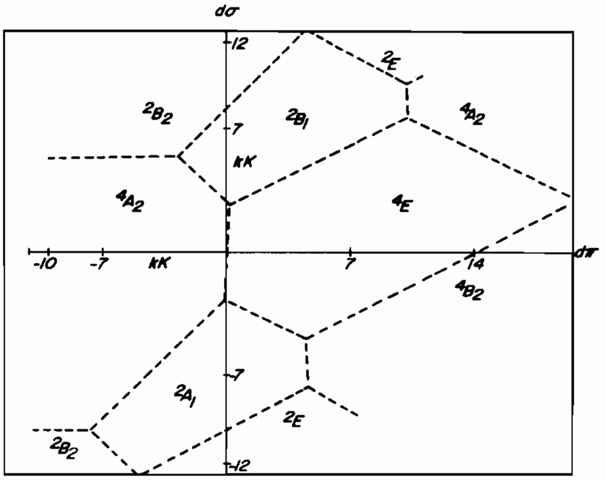

Fig. 6. A ground state energy space diagram for D_{4h}, d^7. DQ = 30000; B = 700; C = 3000 cm^{-1}.

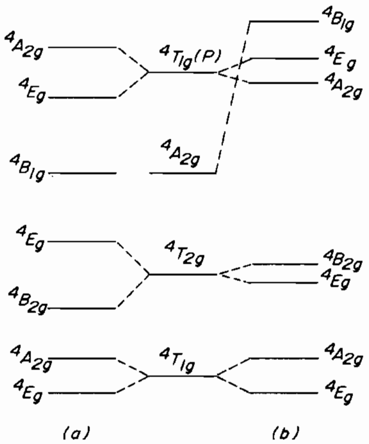

Fig. 7. Splitting diagram for tetragonal d^7 (D_{4h}). a) Energy level sequence for Co(s-Et_2en)$_2X_2$, X = Cl, Br, and Co-(s-Me_2en)$_2(NO_3)_2$. b) Energy level sequence for Co(s-Et_2en)$_2$-$(NCS)_2$.

4.91; 183.3, 16522, 4.92; 200.5, 15230, 4.94; 217.9, 14005, 4.94; 235.1, 13019, 4.95; 253.0, 12135, 4.96; 271.3, 11387, 4.97; 289.6, 10639, 4.965; 298.1, 10334, 4.965. Co(s-Et_2en)$_2(NO_3)_2$ (diamagnetic correction = 226 × 10^{-6} cgs). 80.05, 33562, 4.64; 94.63, 29225, 4.70; 106.8, 26509, 4.76; 123.65, 23413, 4.81; 141.3, 20842, 4.855; 158.8, 18747, 4.88; 176.2, 17034, 4.90; 192.8, 15606, 4.91; 210.6, 14369, 4.92; 246.8, 12373, 4.94; 265.0, 11565, 4.95; 283.2, 10852, 4.96; 301.2, 10187, 4.955; 319.2, 9618, 4.96. Co(s-Me_2en)$_2(NO_3)_2$ (diamagnetic correction = 178.4 × 10^{-6}). 81.25, 34779, 4.755; 100.4, 29195, 4.84; 117.7, 25631, 4.91; 152.7, 20091, 4.955; 170.3, 18159, 4.97; 206.5, 15155, 5.00; 224.9. 13997, 5.02; 243.4, 12924, 5.02; 280.9, 11252, 5.03; 299.1, 10566, 5.03; 318.4, 9923, 5.03; 336.2, 9365, 5.02. Electron spin resonance data were recorded on a 12″ magnet E-Line Varian spectrometer using an Air Products Model LTD-3-110 liquid transfer Heli-Tran refrigerator.

Results and Discussion

Trans Complexes

Tetragonal distortion lifts the degeneracy of the $^4T_{1g}$ ground state of cubic d^7 (Co(II)) to generate the states ^4E_g and $^4A_{2g}$, either of which may now be the ground state in D_{4h} symmetry. A ground state energy space diagram [14, 15] (Fig. 6) shows that these two possibilities are clearly delineated by the sign of the McClure parameter dπ [16]. In this series of complexes with a non-pi bonding ligand in the plane, our initial guess is that dπ would be positive, thus generating a ^4E_g ground state (see Fig. 6). The spectra were in fact fit without constraining the ground term; the best fits were obtained with a ^4E_g ground term as anticipated, in all but one case.

The excited states split according to Fig. 7 but their relative order depends upon the nature of the ligands. The degeneracy of the $^4T_{2g}$ term is lifted in D_{4h} symmetry to generate ^4E_g + $^4B_{2g}$. When DQ(ax) < DQ(eq), the $^4B_{2g}$ term should lie below ^4E_g [1]. For the halogen complexes and Co(sym-Me_2en)$_2$-$(NO_3)_2$ described here DQ(ax) is certainly less than DQ(amine), and the splitting must be as shown in Fig. 7a. Two absorption peaks one near 6–8 kK and the other near 9–11 kK in these complexes can unequivocally be assigned as transitions to $^4B_{2g}$ and to ^4E_g respectively. In the thiocyanate complex DQ(NCS) is comparable to DQ(amine) and no splitting is expected, nor is it observed. Previous calculations [2, 8] of the splitting as a function of field strength have shown that when the $^4T_{2g}$ state splits so that $^4B_{2g}$ < ^4E_g, then the $^4T_{1g}$(P) term splits so that ^4E_g < $^4A_{2g}$ for the range of DQ under consideration here. The chloride and bromide complexes show definitive splitting of the cubic $^4T_{1g}$(P) term into two groups of peaks centred near 17–20 kK and 21–22 kK, whilst Co(sym-Me_2en)$_2(NO_3)_2$ has bands centred near 20 and 23.4 kK. To locate the transition to $^4B_{1g}$ we note that E($^4B_{1g}$) – E($^4B_{2g}$) = 10 Dq-(amine) = *ca.* 12000 cm^{-1} [1, 11]. Thus in the chloride, bromide, and *trans* nitrate complexes $^4B_{1g}$ should lie in the range 18–20 kK.

We may therefore clearly assign the prominent peak in the halogen complexes between 21–22 kK as a transition to $^4A_{2g}$(P). We anticipate that the ^4E_g transition will split [1], though probably not by more than about 500 cm^{-1}. For this reason we prefer to assign the pair of peaks at 18.7 and 19.3 kK, in the bromide, as components of ^4E_g (P), leaving the peak at 17.63 kK assigned to $^4B_{1g}$. A good fit is obtained with this assignment (Fig. 7a), though other

TABLE II. Parameter Data[a] for Cobalt and Nickel Complexes $M(s\text{-}R_2\text{-}en)_2Z_2$.

	Co NCS	Ni NCS	Co Cl	Ni Cl	Co Br	Ni Br	Co(*cis*) NO_3	Ni(*cis*) NO_3	Co(Me) NO_3	Ni(Me) NO_3
DQ	31444	32655	27971	27561	25518	27171	27779	27681	28724	29394
DS	790	−2545	−2966	−5072	−3370	−6777	3038	4140	−4710	−8116
DT	175	−2727	−4701	−4394	−4699	−4383	2803	2655	−3981	−4414
B	780	690	833	864	847	845	767	900	875	887
σ_N	3787	4350	4065	3972	3768	3923	4172	4139	4053	4197
σ_Z	4045	3120	2351	1712	1938	1178	1401	795	1973	1064
π_Z	137	−42	231	−276	144	−644	−268[b]	−795[b]	−275	−925
Δ_1	−274	85	−463	553	−288	1288	−268	−795	550	1850
Δ_2 (Dq-xy)	11360	13050	12196	11914	11304	11768	8897	8991	12160	12590
Δ_3	−516	2460	3429	4519	3658	5489	−2770	−3345	4160	6266
DQ(eq)	31237	35882	33533	32760	31078	32357	24462	24540	33434	34617
DQ(ax)	31858	26202	16846	17163	14398	16799	34412	33964	19303	18949
dσ	193	−923	−1286	−1695	−1372	−2058	1039	1254	−1560	−2350

[a] DQ, DS, DT are NSH parameters [15]. B is the Racah parameter. σ_N, σ_Z, π_Z are OAM parameters [17]. Δ_i are the one electron splitting energies of the d orbitals [1, 28]. DQ(eq) and DQ(ax) are the equatorial and axial global DQ values respectively [15]. The nickel data are abstracted from ref. [1]. The 10 K data were fitted. The complexes are all *trans* except for the species marked (*cis*). All complexes contain $s\text{-}Et_2en$ except for the species marked (Me) which contain $s\text{-}Me_2en$. [b] See Appendix.

permutations of the set of three peaks around 18.7 kK are conceivable. In the more poorly resolved chloride complex, the doublet at 19.89 and 20.21 kK is similarly assigned to ^4E_g (P) and the peak at 19.37 kK to $^4B_{1g}$. In $Co(sym\text{-}Me_2en)_2(NO_3)_2$ the peak at 23.4 kK is clearly assigned to $^4A_{2g}$. The two main peaks near 20 kK in this last complex are probably assignable to $^4B_{1g}$ and ^4E_g, but their order is less secure. Acceptable fits indicating a $^4A_{2g}$ ground term can be obtained with either order, and the parameters so obtained do not differ greatly. Vibronic selection rules [11] for D_{4h} indicate that for a $^4A_2$ ground term, all transitions are allowed in perpendicular polarisation, whilst in parallel polarisation the $^4A_2 \rightarrow {}^4B_1$ transition is both electronically and vibronically forbidden. Since the 19960 cm^{-1} band is absent in one polarisation, this would appear to favour its assignment to $^4B_1$. There is the possibility that the two peaks are components of ^4E_g but the splitting is rather large for this eventuality.

We now consider the thiocyanate complex, with these arguments in mind. It is evident that the peaks at 19 and 20–21 kK are too low in energy to be assigned to $^4B_{1g}$. We therefore assign the well defined shoulder at 21.7 kK to this transition. The two aforementioned peaks are then readily assigned as $^4A_{2g}$(P) and ^4E_g(P) respectively, the latter, as expected for a doubly degenerate transition, being the more intense (Fig. 7b).

In this fashion the various transitions are almost unequivocally located before detailed calculations are undertaken. In fact these choices gave good fits immediately. Other possibilities were investigated but most gave poor fits or unacceptable parameter values. The remaining weaker features in the spectrum are probably quartet–doublet transitions, and possibly spin–orbit or vibrational components.

The data were processed utilising the Normalised Spherical Harmonic Hamiltonian (NSH) [15] formalism, with the four variables, DQ, DS, DT and B. Five bands are fitted by these four variables in each case. These parameters are then converted into the McClure parameters, orbital angular overlap (OAM) [17], and ligand field parameters through standard formulae [15]. The results are displayed in Table II where they are compared with the corresponding nickel data. There is generally good agreement between the weaker features of the spectra, and the calculated energies of quartet–doublet transitions, but no attempt has been made to fit these. All the complexes are best fitted with a ^4E_g ground term with the exception of $Co(s\text{-}Me_2en)_2(NO_3)_2$. This last complex is best fitted with a $^4A_{2g}$ ground term, but possible fits with a ^4E_g ground term were not so inferior. Further data are necessary to clarify the issue.

The NSH procedure is appropriate for computer processing of the spectra of low symmetry complexes [15], but the orbital angular overlap model is of more direct utility in assessing the chemical significance of the parameter set. Unlike nickel(II) there is, as yet, no definitive body of OAM data for cobalt(II), to be used for comparative purposes. We summarise in Table III available OAM data for cobalt(II) complexes based on electronic spectra and/or magnetic investigations; we also include some analogous nickel(II) complexes to demonstrate the very rough equivalence between the two data sets.

TABLE III. Selected OAM Data for Some Cobalt(II) and Nickel(II) Complexes (cm^{-1}).

σ_Z	π_Z	σ_N	π_N	Species[a]	Ref.
–	–	2754	–1184	bis(PCD)Co(II)	29
3000(Cl)	250(Cl)	3700	100	$CoPy_4Cl_2$	2
3000(Br)	600(Br)	3700	100	$CoPy_4Br_2$	2
–	–	4300(σ_0)	665, 1330[b](σ_0)	$Co(PyO)_6^{++}$	30
3700	200, 200	3700	125	$CoPy_4(NCS)_2$	7
2300	0	–	–	$CoCl_4^{=}$	31
4000	0	2500	–	$Co_2(benzoate)_2Q_2$	36
4200(σ_0)	1300, 900 (π_0)	3600, 2100[c]	900, 0	$Ni(sal\text{-}I)_2$	32
4200(σ_0)	660, 1000 (π_0)	3800	930	$Ni(sal\text{-}II)_2$	33
–	–	4393	830, 1660[b]	$Ni(PyO)_6^{++}$	34
2980	540	4670	570	$Nipy_4Cl_2$	35
2450	340	4500	500	$NiPy_4Br_2$	35
1370		3870[ef]		$Ni(MPZ)_4Cl_2$	38
740		3690[eg]		$Ni(MPZ)_4B\nu_2$	38
2123	–409	4010	0	$Ni(en)_2(NCS)_2$	39
3843	125	3583	0	$Ni(NH_3)_4(NCS)_2$	39

[a] PCD = N-t-butylpyrrole-2-carbaldiimine; Sal-I = 5-chloro-N-β-diethylaminoethylsalicylideneiminato; PyO = pyridine N-oxide; Sal-II = N-isopropylsalicylideneiminato. MPZ = 5-methylpyrazole; Q = quinoline. [b] Two orthogonal parameters, pi-x and pi-y. [c] In-plane and apical nitrogen bond resp. [d] Calculated data. [e] $d\sigma = -1874$, $d\pi = -515$. [f] $d\sigma = -2211$, $d\pi = -852$ cm^{-1}.

A value [37] of sigma-xy of 8546 cm^{-1} for high spin Co(3MeO-Salen)·H_2O seems significantly out of line with relevant data quoted above.

This data base also serves to identify the approximate values of σ_N and σ_Z to be anticipated in the ethylenediamine series, in association with the OAM spectrochemical series [18]. Our values of σ_N (N = amine, NCS) (Table II) are certainly compatible with those previously published. The values of σ_{Cl} and σ_{Br} are also acceptable, though on the low energy side of those previously reported. However some of the literature values are subject to considerable uncertainty (see refs. in Table III for details). The π_Z values are small and compatible with previous experience. We conclude therefore that our derived parameter set is consistent with the available literature.

The OAM parameters are a measure of the anti-bonding character of the d orbitals. It has generally been assumed that the larger these parameters, the stronger is the relevant bonding term. This correlation however should be treated with caution [19]. The in-plane sigma anti-bonding around the metal is comparable for both cobalt(II) and nickel(II), but the axial sigma anti-bonding σ_Z is very significantly greater for cobalt than for nickel. The value of π_Z is also consistently larger for cobalt than for nickel, though the parameters are generally small [1]. Both these observations are fully consistent with the relative configurations $\pi^{*4}\delta^{*2}\sigma^{*2}$ for nickel and $\pi^{*3}\delta^{*2}\sigma^{*2}$ for cobalt. The extra π^* electron in nickel(II) causes a greater repulsion between the metal ion and pi-bonding axial ligand causing a relative reduction in both σ_Z and π_Z.

Indeed this same conclusion may be drawn from corresponding data for cubic complexes, CoL_6 and NiL_6. With pi-bonding ligands DQ (L, Co) is almost invariably 5–12% larger than DQ (L, Ni). For non-pi bonding ligands DQ (L, Co) ≅ DQ (L, Ni) though there are some exceptions [11]. In the tetragonal complexes the effect operates on two ligands whilst in the octahedral complexes it is shared over six ligands; hence it is more obvious in the former series. Note that this sigma anti-bonding variation is obscured in the DQ_Z values because of the concomitant variation of π_Z. This is a compelling example of the kind of additional bonding information which can be derived from study of suitable low symmetry systems. It is curious that whilst the π^* occupation argument provides a simple explanation of the relative magnitudes of the axial sigma interaction, the pi-parameters themselves are very small.

Cis Complexes

In the nickel series $Ni(s\text{-}Me_2en)_2(NO_3)_2$ is *trans* whilst $Ni(s\text{-}Et_2en)_2(NO_3)_2$ is *cis* [1, 20]. We have already seen that $Co(s\text{-}Me_2en)_2(NO_3)_2$ is *trans.* The

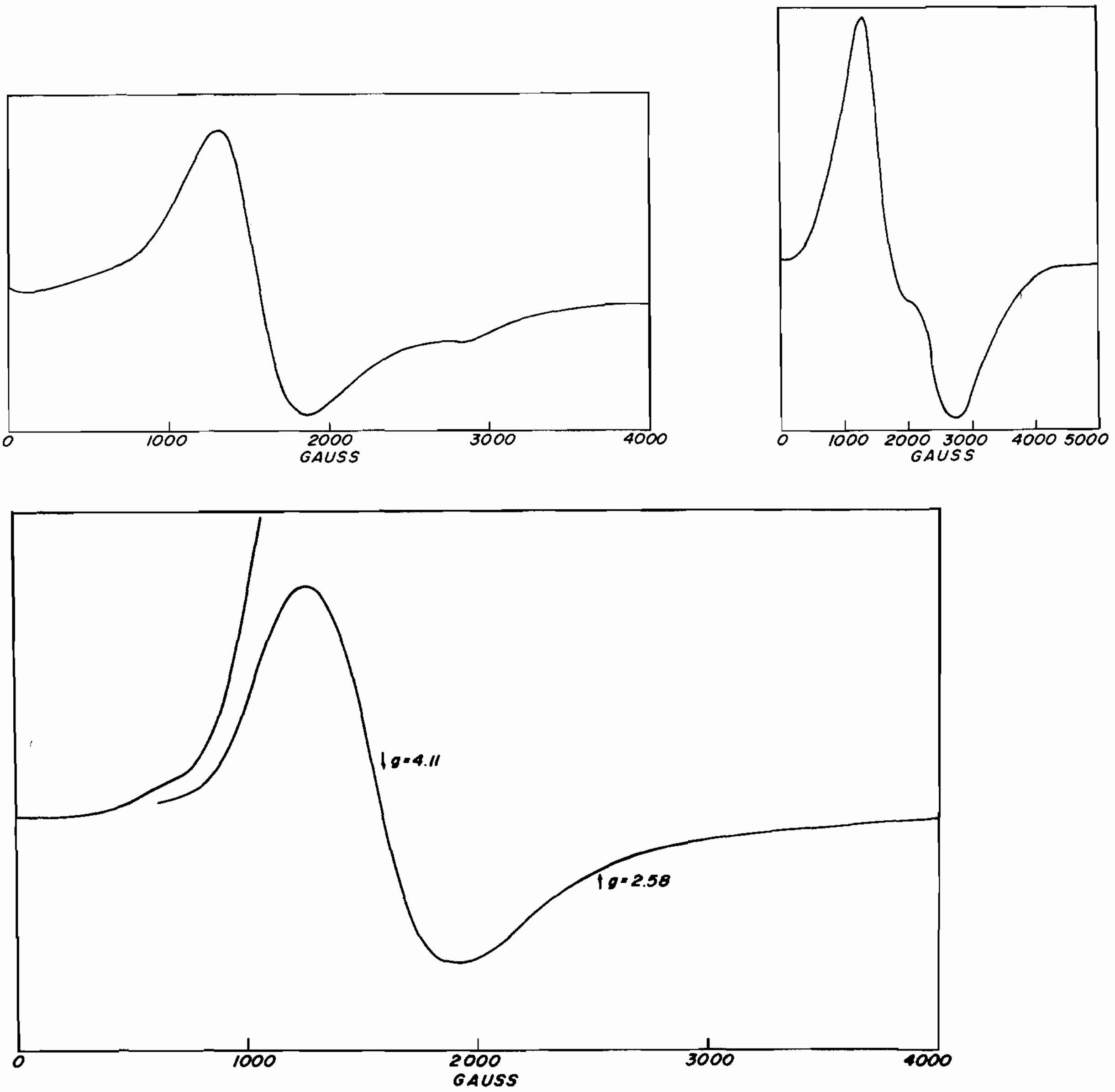

Fig. 8. a) The Esr spectrum of $Co(s\text{-}Et_2en)_2Cl_2$ in a CH_3CN glass at 4 K. Power = 1 mw; Gain = 250; Modulation amplitude = 5 gauss; Frequency = 9.1605 GHz. b) The Esr spectrum of $Co(s\text{-}Et_2en)_2Br_2$ in a CH_3CN glass at 4 K. Power = 5 mw; Gain = 250; Modulation Amplitude = 8 gauss; Frequency = 9.1745 GHz. c) The Esr spectrum of $Co(s\text{-}Et_2en)_2(NO_3)_2$ in a CH_3CN glass at 4 K. Power = 1 mw; Gain = 800; Modulation amplitude = 6.3 gauss; Frequency = 9.150 GHz.

infrared spectra of $M(s\text{-}Et_2en)_2(NO_3)_2$ (M = Co, Ni) are very similar [12], and, as demonstrated in Fig. 5, $Co(s\text{-}Et_2en)_2(NO_3)_2$ does not exhibit the magnitude of splitting of the bands near 20 kK which would now be anticipated for a *trans*-derivative (see Fig. 4). We therefore analyse this system in terms of cis symmetry.

We present a detailed study of *cis* NiN_4Z_2 complexes elsewhere [20], and present only a brief discussion here. The $[Co(s\text{-}Et_2en)_2(NO_3)]^+$ cation(II) may be considered pseudo-tetragonal with a NCoN axis and a N_2CoO_2 equatorial plane. We assume effective (intermediate) D_{4h} symmetry and expect DQax > DQeq, DT positive, and $E(T_2) < B_2(T_2)$. We also anticipate $d\sigma$ +ve, and $d\pi$ +ve (π_0 negative, see Appendix) if NO_3^- has some pi-accepting character. Using Fig. 6 this analysis predicts a ^4E ground term.

The lower energy absorption peaks near 10 kK (Fig. 5) are now readily assigned to the transitions to $^4E(T_2)$ and $^4B_2(T_2)$ respectively. With this sequence we expect the ^4P term to split, $^4A_2(T_1(P)) < {}^4E(T_1(P))$. There are three main features in the 17–22 kK region which we iterate using each alternate assignment, to an acceptable fit. The results are shown in Tables I, II. Values of the OAM parameters are calculated using the method for *cis* complexes outlined in the Appendix. We note that the axial DQ (NCoN axis) and corresponding σ_N value is in good agreement with the corresponding (equatorial) values deduced from the *trans* data.

The nitrate values are only approximate since our treatment assumes an orthoaxial chromophore which is not the case here. The available data do not merit more detailed analysis, which would require an additional variable. We note however that the OAM parameters for the *cis* nitrate are comparable to the values found both for the *trans* s-Me$_2$en nitrate discussed here, and for the *cis* nickel analog (Table III) [20]. If we consider the DQ(eq)(amine) and DQ(ax) (NO$_3$) values for the *trans* nitrate (above), then the average of these numbers, namely 26368 cm^{-1}, should approximate to the DQ(eq) value of the *cis*-nitrate complex ($CoN_2(NO_3)_2$) plane, namely 24462 cm^{-1}; the agreement is quite satisfactory. Note that in this *cis*-example, compared with its nickel analog (Table II), $\sigma_{NO_3(Co)} > \sigma_{NO_3(Ni)}$ which is consistent with the *trans* complex series, $\sigma_{Z(Co)} > \sigma_{Z(Ni)}$ given that the principal axis of the molecule now passes through the nitrate group.

Electron Spin Resonance and Magnetic Data

We report esr and magnetic data for these complexes. The esr data at liquid helium temperature are displayed in Fig. 8. Data for tetragonally distorted high spin cobalt(II) can only be observed at very low temperatures and are not common in the literature [21–25]. The overall esr spectra of these complexes are similar to those described earlier but they do not display hyperfine structure. The chloride complex exhibits absorption at $g_\parallel = 2.32$, $g_\perp = 4.116$. In the bromide complex absorption is centred at $g = 3.3$. The *cis* nitrate has an esr spectrum ($g_\parallel = 2.58$, $g_\perp = 4.11$) very similar to those of the halides. This similarity may be taken as corroboratory evidence that these three complexes possess the same ground term, ^4E. Some early studies [21] demonstrated permissible ranges for $g_\parallel$ and $g_\perp$ in terms of the splitting of the $^4T_{1g}$ term and coupling to excited states. Our complexes are close to, but do not fit exactly into this prescribed range (see Fig. 3 of ref. 21a), precluding a simple calculation of the ground term splitting and even a determination of its sense. There is rhombic distortion in these complexes as is evident from their electronic spectra (splitting of E states). This is undoubtedly a cause of their poor behaviour [21, 26].

Magnetic data for these complexes recorded down to 80 K are reported in the Experimental section. These data are fully consistent with the tetragonal distortion in these derivatives. Although a general solution to the theoretical treatment of this problem (d^7, high spin, D_{4h}) has been published [27] we do not attempt a detailed analysis. It is well known that such an analysis is relatively insensitive to the magnitude, or indeed sign, of the splitting of the $^4T_{1g}$ term, unless very low temperature data and/or magnetic anisotropy data are available.

Acknowledgments

ABPL and IMW are indebted to the National Research Council (Canada) for financial support. We are also indebted to the California Institute of Technology for generous use of their esr and liquid helium facility. PM acknowledges a grant from the Research Corporation for the purchase of the Displex Cryogenic Refrigerator.

References

1 A. B. P. Lever, G. London and P. J. McCarthy, *Can. J. Chem., 55,* 3172 (1977).

2 M. Gerloch, R. F. McMeeking and A. M. White, *J. Chem. Soc. Dalton,* 655 (1976).

3 A. B. P. Lever and D. Ogden, *J. Chem. Soc. A,* 2041 (1967).

4 J. Catterick and P. Thornton, *J. Chem. Soc. Dalton,* 1634 (1976).

5 A. Bencini, C. Benelli and D. Gatteschi, *Inorg. Chem., 17,* 3313 (1978).

6 M. Gerloch, J. Kohl, J. Lewis and W. Urland, *J. Chem. Soc. A,* 3283 (1970).

7 M. Gerloch, R. F. McMeeking and A. M. White, *J. Chem. Soc. Dalton,* 2452 (1975).

8 M. Ciampolini and I. Bertini, *J. Chem. Soc. A,* 2241 (1968).

9 R. L. Carlin, C. J. O'Connor and S. N. Bhatia, *J. Am. Chem. Soc., 98,* 685 (1976).

10 J. Ferguson, T. E. Wood, and H. J. Guggenheim, *Inorg. Chem., 14,* 177 (1975); J. Ferguson and T. E. Wood, *Inorg. Chem., 14,* 183 (1975); J. Ferguson and T. E. Wood, *Inorg. Chem., 14,* 190 (1975).

11 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, 1968.

12 A. B. P. Lever and E. Mantovani, *Can. J. Chem., 51,* 1567 (1973).

13 J. C. Donini, B. R. Hollebone, R. A. Koehler and A. B. P. Lever, *J. Phys. E., 5,* 385 (1972).

14 J. C. Donini, B. R. Hollebone and A. B. P. Lever, *J. Am. Chem. Soc., 93,* 6455 (1971).

15 J. C. Donini, B. R. Hollebone and A. B. P. Lever, *Prog. Inorg. Chem., 22,* 226 (1977).

16 D. S. McClure, in 'Advances in the Chemistry of the Coordination Compounds', edited by S. Kirschner, Macmillan, New York, 1961.

17 C. E. Schaffer, *Struct. and Bond.*, *5*, 68 (1968).
18 J. Glerup, O. Monsted and C. E. Schaffer, *Inorg. Chem.*, *15*, 1399 (1976).
19 J. K. Burdett, *J. Am. Chem. Soc.*, *101*, 580 (1979).
20 A. B. P. Lever, I. M. Walker and P. J. McCarthy, to be submitted for publication.
21 a) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. A*, *206*, 173 (1951). b) J. S. Griffith, 'Theory of the Transition Metal Ions', Cambridge U.P., 1964, p. 362.
22 B. Bleaney and D. J. Ingram, *Proc. Roy. Soc. A*, *208* 143 (1951).
23 W. Low, *Phys. Rev.*, *109*, 256 (1958).
24 J. W. Orton, P. Auzins, J. H. E. Griffiths and J. E. Wertz, *Proc. Phys. Soc. (London)*, *78*, 554 (1961).
25 J. Reedijk and P. J. van der Put, *Proc. XVI ICCC (Dublin)* 1974, paper 2.27b.
26 W. Gehlhoff, *Physic. Status Solidi, B*, *80*, 549 (1977).
27 B. N. Figgis, M. Gerloch, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc.*, 2086 (1968).
28 A. B. P. Lever, *Coord. Chem. Rev.*, *3*, 119 (1968).
29 I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chim. Acta*, *13*, 145 (1975).
30 D. J. Mackay, S. V. Evans, and R. F. McMeeking, *J. Chem. Soc. Dalton*, 160 (1978).
31 W. De W. Horrocks and D. A. Burlone, *J. Am. Chem. Soc.*, *98*, 6512 (1976).
32 D. A. Cruse and M. Gerloch, *J. Chem. Soc. Dalton*, 1613 (1977).
33 D. A. Cruse and M. Gerloch, *J. Chem. Soc. Dalton*, 152 (1977).
34 D. J. Mackay and R. F McMeeking, *J. Chem. Soc. Dalton*, 2186 (1977).
35 M. A. Hitchman, *Inorg. Chem.*, *11*, 2387 (1972).
36 P. D. Boyd, J. E. Davies, and M. Gerloch, *Proc. Roy. Soc., Ser. A*, *360*, 191 (1978).
37 M. A. Hitchman, *Inorg. Chim. Acta*, *26*, 237 (1977).
38 P. J. McCarthy and J. Reedijk, unpublished results.
39 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, *15*, 203 (1976).

Appendix

The equations appropriate for *cis* complexes are developed in ref. 20. We report relevant expressions here, based upon the assumption of pseudo D_{4h} symmetry. The nitrate group is assumed to be orthoaxial, in so far as the oxygen ligands are concerned, and the angles in the plane are assumed to be 90°. Further the magnitude of the σ_N anti-bonding interaction along the NCoN pseudo tetragonal axis is presumed to be the same as the value of σ_N in the pseudo tetragonal plane, *trans* to nitrate. Then:

$d\sigma = (3/4)(0.5\ \sigma_N - 0.5\ \sigma_O)$
$d\pi = 0.5\ \pi_N - 0.5\ \pi_O$
$\sigma_N = 0.12123\ DQ(ax)$
$\sigma_O = \sigma_N - (8/3)\ d\sigma$
$\pi_O = -2\ d\pi$

A more sophisticated approach recognising that these complexes belong to the point group C_{2v}, and that the angle subtended by the nitrate group at the metal atom, is not 90°, will be published elsewhere [20].