EPR and ENDOR Studies of Charge Transfer Interaction of Cobalt(II) and Copper(II) Porphyrins with π Donors and Acceptors

MASAMOTO IWAIZUMI, YASUNORI OHBA

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan

HIDEKI IIDA* and MASATOSHI HIRAYAMA

Department of Chemistry, Faculty of Science, Ibaraki University, Mito 310, Japan

Received May 24, 1983

EPR spectra of cobalt(II) complexes of octaethylporphyrin and tetraphenylporphyrin, CoOEP and CoTPP, are strongly affected by interactions with π electron donors or acceptors, the effects of the interaction being generally larger in CoOEP than in CoTPP. Much smaller but still significant effects of charge transfer complex formations were observed also on EPR and ENDOR spectra of copper(II) porphyrins, CuOEP and CuTPP. Direct charge transfer interactions between the metal d orbitals and the π donors or acceptors make important contributions to the perturbation of the metal d orbital states by the charge transfer complex formation.

Introduction

Charge transfer (CT) complex formation of metal complexes with electron donors or acceptors has drawn extensive interest, and especially CT interactions containing porphyrin complexes have been widely investigated [1] because of importance of porphyrin complexes in biological systems, and because of their tendency to dimerization or aggregation. However, little information has been obtained on how the electronic structures of metal complexes are affected by the CT complex formation with π donors or acceptors. The present work concerns an attempt to elucidate such effects on cobalt(II) and copper(II) complexes of octaethylporphyrin (H_2OEP) and tetraphenylporphyrin (H_2-TPP) using EPR and ENDOR spectroscopy.

The effects of CT complex formation of EPR spectra of metalloporphyrins have been shown by Walker [2] and Yokoi *et al.* [1(k)]. Yokoi *et al.* examined the effects of interaction with some π acceptors on the EPR spectra of CuOEP and observed small but non-negligible changes in the spectra. Walker observed much more drastic effects on the EPR spectra for tetra-*p*-tolylporphyrinatocobalt(II), CoMeTPP. In these papers, however, it is not clearly shown how the d orbital states are perturbed by the CT complex formation.

Experimental

Materials

CoOEP, CoTPP, CuOEP and CuTPP were prepared and purified according to literature [3]. Toluene used as a solvent was purified by distillation from sodium metal. E.p. grade pyridine was distilled twice from sodium hydroxide. Both toluene and pyridine were stored over a molecular sieve on a vacuum line after degassing. S.p. grade 1,3,5-trinitrobenzene (TNB) was purified by recrystallization from ethanol and dried *in vacuo*. S.p. grade pyrene was purified by sublimation. Nitrobenzene (NB), 2,4-dinitrofluorobenzene (DNFB), *m*-nitrobenzotrifluoride (NBTF) were purified by vacuum distillation. S.p. grade *m*-dinitrobenzene (DNB), *o*-nitrophenol (NPH), 2,4-dinitrophenol (DNPH), 2,4,6-trinitrophenol (TNPH), 9-fluorenone (FL), 2,4,7-trinitro-9-fluorenylidenemalonitril(TNFMN), 2,4,5,7-tetranitro-9-fluorenone (TNF), *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) were used without further purification. Doped samples of the cobalt porphyrins in diamagnetic metal (Mg(II), Ni(II), and Zn(II)) complexes of H_2OEP and H_2TPP, abbreviated as Co/MOEP and Co/MTPP (M = Mg, Ni, or Zn), were prepared by co-precipitation of the cobalt and diamagnetic metalloporphyrins in the mole ratio of 1:100 from toluene or benzene solutions. The metalloporphyrins used as host molecules were prepared and purified according to the literature [3]. Sample solutions of the cobalt(II) complexes were prepared on a vacuum line.

---

*Present address: Suzaka High School. Suzaka 382, Japan.

0020-1693/84/$3.00

© Elsevier Sequoia/Printed in Switzerland

TABLE I. EPR Parameters for CoOEP.

added donor or acceptor	solvent or matrix	$g_\perp$	$g_\parallel$	$\lvert^{Co}A_\perp\rvert/h$ MHz	$\lvert^{Co}A_\parallel\rvert/h$ MHz
–	NiOEP	3.39	1.55	1390	610
TNFMN	toluene	3.35	1.60	1300	530
–	MgOEP[a]	3.28	1.79	1138	497
		3.25	1.79	1118	497
TNPH	toluene	3.25	1.76	1145	540
TNB	toluene	3.21	1.78	1110	505
–	ZnOEP[a]	3.12	1.87	929	445
		3.04	1.88	906	441
DNFB	toluene	3.01	1.90	860	452
DNB	toluene	2.93	1.92	796	438
DNPH	toluene	2.88	1.94	726	446
FL	toluene	2.88	1.94	721	432
NBTF	toluene	2.85	1.94	700	425
NB	toluene	2.83	1.95	689	425
–	toluene	2.82[b]	1.96	646	413
		2.97[c]	1.92	815	434
pyrene	toluene	2.46	2.00	257	328
TMPD	toluene	2.46	2.01	217	302
pyridine	toluene	2.33[d]	2.03	<45	230
		2.23[e]	?	150	?

[a] Signals from different sites were observed. [b] 1:1 complex? [c] 2;1 complex? [d] 1:1 complex. [e] 2:1 complex.

Physical Measurements

EPR measurements were performed at 50–70 K using a Varian E 112 EPR spectrometer for the toluene solutions of the cobalt and copper porphyrins containing large excess of π donors or acceptors, and for the doped samples. ENDOR measurements were prepared for the toluene solutions of the copper complexes using a Varian E 1700 ENDOR spectrometer at 20 K. The temperatures were controlled by a helium gas flow cryostat.

Results and Discussion

CT Interation of CoOEP and CoTPP

The EPR spectra of CoOEP and CoTPP show drastic changes in the presence of π donors or acceptors, as Walker has previously observed for CoMeTPP [2]. Superimposed spectra of two species were observed for several cases. Some of them are attributed to formation of 1:1 and 2:1 complexes with added acceptors or donors. In the case of the toluene solutions of CoOEP and CoTPP containing pyrene and of the CoTPP containing TMPD, superimposed patterns are attributed to the presence of the species complexed with the solvent toluene molecules and those complexed with the co-existing π molecules.

By addition of TNF, TCNE and TCNQ to the CoOEP solutions, EPR signals due to CoOEP disappeared and signals attributable to the free radicals were observed, indicating the formation of cobalt(III) complexes and anion radicals of the acceptors. Similar reactions were also observed for the CoTPP solutions by addition of TCNE and TCNQ, but TNF did not oxidize CoTPP, in contrast with the case of CoOEP.

The EPR parameters determined by the second order perturbation analysis are listed in Tables I and II in the order of decreasing g values. The Tables also contain data for the complexes with pyridine, which is a sigma donor.

The changes of the g and hf coupling parameters observed for the toluene solutions seem to be related to the nature of the CT interaction: the interaction with stronger electron acceptors gives larger $g_\perp$, $A_\perp^{Co}$, and $A_\parallel^{Co}$ and smaller $g_\parallel$ values, and *vice versa* for the interaction with electron donors. Tables I and II show also that the changes of EPR parameters of CoTPP are generally smaller than those in the CoOEP system, indicating that the CT interaction in CoTPP is weaker than in CoOEP, on account of the presence of phenyl rings at the meso positions having conformation normal to the porphyrin ring [4]. The less reactivity to the formation of the cobalt(III) complex by TNF in the CoTPP system is also attributed to the presence of the phenyl rings. It should be noticed that the cobalt(II) porphyrins doped in the diamagnetic metal porphyrins show EPR

TABLE II. EPR Parameters for CoTPP.

added donor or acceptor	solvent or matrix	$g_\perp$	$g_\parallel$	$\lvert{}^{Co}A_\perp\rvert/h$ MHz	$\lvert{}^{Co}A_\parallel\rvert/h$ MHz
–	NiTPP	3.35	1.73	1245	542
–	ZnTPP	3.30	1.75	1190	518
TNPH[a]	toluene	3.19	1.80	1100	491
TNB[a]	toluene	3.17	1.82	1060	490
DNFB[b]	toluene	3.13	1.85	1000	483
DNB[a]	toluene	3.09	1.85	967	474
FL[c]	toluene	2.80	1.96	650	422
TNF[c]	toluene	2.92	1.93	767	430
TNFMN[c]	toluene	2.91	1.93	752	436
NB[c]	toluene	2.81	1.95	648	426
–	toluene[c]	2.75	1.95	612	416
NPH	toluene	2.63	1.99	440	375
pyrene	toluene	2.45	2.00	270	335
TMPD	toluene	2.45	2.01	220	295
pyridine	toluene	2.32[b]	2.02	<45	235
		2.23[d]	2.04	150	175

[a] 2:1 complex? [b] 1:1 complex? [c] 1:1 complex. [d] 2:1 complex.

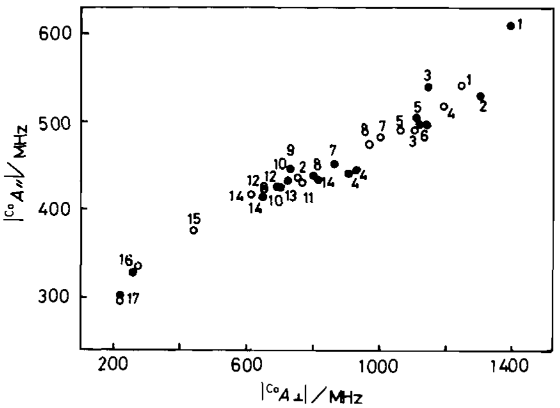

Fig. 1. Plot of ${}^{Co}A_\parallel$ *vs.* ${}^{Co}A_\perp$. The marks ● and ○ are for CoOEP and CoTPP interacting with 1: NiOEP or NiTPP, 2: TNFMN, 3: TNPH, 4: ZnOEP or ZnTPP, 5: TNB, 6: MgOEP or MgTPP, 8: DNFB, 8: DNB, 9: DNPH, 10: FL, 11: THF, 12: NB, 13: NBTF, 14: toluene, 15: NPH. 16: pyrene, and 17: TMPD, respectively.

spectra with larger $g_\perp$, $A_\perp{}^{Co}$, and $A_\parallel{}^{Co}$ and smaller $g_\parallel$ values than those in toluene solutions.

Effects of CT Complex Formation on Electronic States of Cobalt

Figure 1 shows linear correlation between the observed $A_\parallel{}^{Co}$ and $A_\perp{}^{Co}$. According to the 1st order approximation, $A_\parallel{}^{Co}$ and $A_\perp{}^{Co}$ are expressed as [5]

$$A_\parallel{}^{Co} = -K + \frac{P}{7}\,[4 + 6C_1 + 4(C_2 - C_3)] \tag{1}$$

$$A_\perp{}^{Co} = -K - \frac{P}{7}\,[2 + 45C_1] \tag{2}$$

where K and P are isotropic and anisotropic hf interactions and C_1, C_2 and C_3 are given by,

$$C_1 = \frac{\xi}{\Delta E[^2E(1)]}\,, \qquad C_2 = \frac{\xi}{\Delta E[^4E]}\,,$$

$$C_3 = \frac{\xi}{\Delta E[^2E(2)]}\,. \tag{3}$$

ξ is a spin–orbit coupling parameter. The energy differences are expressed using one electron ligand field energies and Racah parameters as

$$\begin{aligned} \Delta E[^2E(1)] &= E(z^2) - E(xz, yz) + 5B \\ \Delta E[^4E] &= E(xy) - E(xz, yz) - 4(B + C) \\ \Delta E[^2E(2)] &= E(xy) - E(xz, yz) + 4B - C \end{aligned} \tag{4}$$

Therefore, the linear correlation between $A_\parallel{}^{Co}$ and $A_\perp{}^{Co}$ suggests that the changes in $A_\parallel{}^{Co}$ and $A_\perp{}^{Co}$ arise mainly from changes in the K and C_1 terms, and the $(C_2 - C_3)$ term does not make a significant contribution. This implies that the d orbitals significantly perturbed by the CT complex formation are d_{z^2}, d_{xz} and d_{yz} [6].

In order to consider in more detail the effects on the d orbital states of cobalt, the calculations made by Lin [7] on the electronic structures of some cobalt porphyrins are relevant. Lin pointed out the

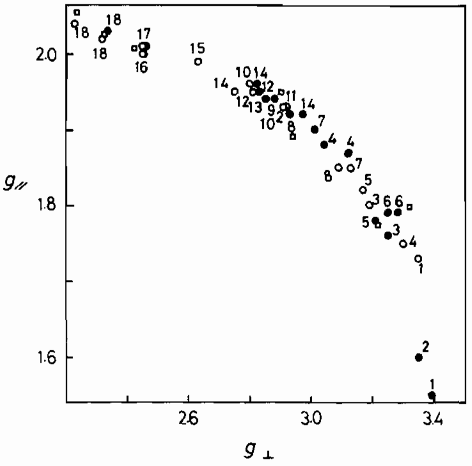

Fig. 2. Plot of $g_\parallel$ *vs.* $g_\perp$ for cobalt porphyrins. The marks ● and ○ are for CoOEP and CoTPP interacting with 1: NiOEP or NiTPP, 2: TNFMN, 3: TNPH, 4: ZnOEP or ZnTPP, 5: TNB, 6: MgOEP or MgTPP, 7: DNFB, 8: DNB, 9: DNPH, 10: FL, 11: TNF, 12: NB, 13: NBTF, 14: toluene, 15: NPH, 16: TMPD, 17: pyrene, and 18: pyridine, respectively. The marks ▫ are for the data taken from ref. 7.

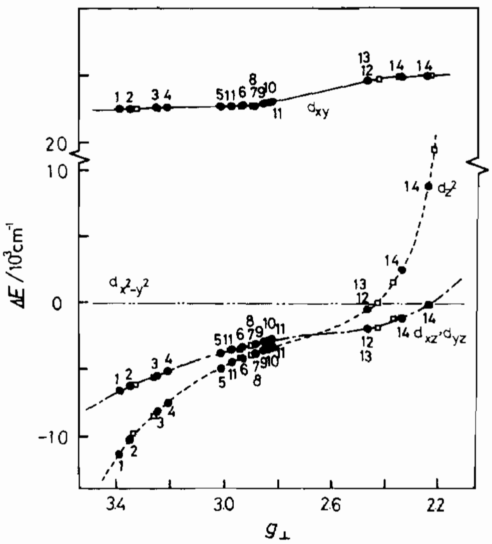

Fig. 3. Plot of the relative d orbital energies *vs.* $g_\perp$. The marks ● are for CoOEP interacting with 1: NiOEP, 2: TNFMN, 3: TNB, 4: DNFB, 5: DNB, 6: DNPH, 7: FL, 8: NB, 9: toluene, 10: pyrene, 11: TMPD, and 12: pyridine, respectively. The marks ▫ are for the complexes treated in ref. 7.

importance of mixing low-lying quartet states to the ground state to explain the observed $g_\parallel$ values, and constructed the ground electronic states by diagonalizing the matrix of the combined ligand field, electrostatic, and spin–orbit coupling energy, instead of using the perturbation technique. As Fig. 2 shows, the experimental data used in his calculation fit the correlation among the data in the present system, indicating that his calculation is applicable to the present complex system. We estimate, therefore, relative d orbital levels in each complex by referring Lin's theoretical treatment on $g_\perp$ values, instead of doing laborious calculations for each case.

Figure 3 shows plots of the d orbital energies against the $g_\perp$ values. The curves are drawn by connecting Lin's data by assuming the $d_{x^2-y^2}$ level to be constant. The points for the complexes in the present work are plotted on the curves based on the observed $g_\perp$ values. It should be noticed that the decrease of d_{z^2} level below d_{xz}, d_{yz} or $d_{x^2-y^2}$ seen in Fig. 3 does not immediately mean that the unpaired electron orbital in the ground states changes from d_{z^2} to the others, because effects of interelectron repulsion can make the $^2A_1(d_{z^2})$ state still ground state [7, 8].

Figure 3 indicates that the d_{z^2} level in the doped samples is very low. X-ray crystallographic analyses indicate that there is space above the central metal of the complexes in the crystals [9], and hence direct interaction of the central metals with the surrounding molecules is considered to be very small. Therefore, the marked lowering of the d_{z^2} level in the doped samples may be mainly attributed to a decrease of electrorepulsive potential field from the surrounding molecules to the metal d electrons.

In solutions, however, donor, acceptor or solvent molecules are situated near the metals and they will impose electrorepulsive fields on the metal d orbitals, elevating the levels, (especially those of d_{z^2}). However, the good correlation observed between the EPR parameters and the electron donor or acceptor properties of the interacting π molecules suggests that the CT interaction with the π donors or acceptors appreciably affect the metal d orbital states. As is shown in Fig. 3, the interaction of the metal d orbitals with π acceptors in solution lowers the d_{z^2}, d_{xz} and d_{yz} levels, in the order of $d_{xz} \sim d_{yz} < d_{z^2}$, and *vice versa* for the interaction with the π donors.

Previously La Mar *et al.* examined effects of CT complex formation with TNB on the d orbital state of CoMeTPP using the NMR spectroscopy [1(h)]. They showed that the d_{z^2} level lowers by the interaction with TNB and explained it by considering CT from the porphyrin π orbitals to TNB; it causes decrease of σ electron donation from the porphyrin ligand to the cobalt, resulting in stabilization of the d_{z^2} level. However, their model does not explain why the σ type d_{z^2} orbital is more affected by the CT interaction than the π type d_{xz} and d_{yz} orbitals and why the changes of σ electron donation from the porphyrin ring does not affect the d_{xy} orbital more, having larger overlap with the porphyrin σ orbitals. In the CT interaction of the metalloporphyrins, the

TABLE III. EPR and ENDOR Parameters for CuOEP in Toluene.

added donor or acceptor	$g_\parallel$	$\lvert {}^{Cu}A_\parallel \rvert/h$ MHz	${}^{N}A_\perp/h^a$ MHz	${}^{N}A_d/h$ MHz	${}^{N}A_i/h$ MHz	${}^{H}A_\perp/h^a$ MHz	${}^{H}A_d/h$ MHz	${}^{H}A_i/h$ MHz
TNPH	2.183	622	44.6	−0.79	45.4	1.58	−0.74	2.32
TNF	2.183	622	44.5	−0.79	45.2	1.58	−0.74	2.32
TNB	2.184	616	44.3	−0.79	45.1	1.58	−0.74	2.32
–	2.187	615	43.8	−0.79	44.5	1.55	−0.74	2.29
pyridine	2.213	574	41.5	−0.80	42.4	1.49	−0.75	2.24

[a] Sign of the coupling constants is taken to be positive according to Brown and Hoffman [10].

TABLE IV. EPR and ENDOR Parameters for CuTPP in Toluene.

added donor or acceptor	$g_\parallel$	$\lvert {}^{Cu}A_\parallel \rvert/h$ MHz	${}^{N}A_\perp/h^a$ MHz	${}^{N}A_d/h$ MHz	${}^{N}A_i/h$ MHz	${}^{H}A_\perp/h^a$ MHz	${}^{H}A_d/h$ MHz	${}^{H}A_i/h$ MHz
TNPH	2.184	620	44.1	−0.79	44.9	0.49	−0.47	0.96
TNB	2.185	616	43.9	−0.79	44.7	0.49	−0.47	0.96
TNF	2.190	615	43.6	−0.79	44.4	0.47	−0.48	0.95
–	2.192	613	43.6	−0.79	44.4	0.47	−0.48	0.95
pyrene	2.192	613	43.6	−0.79	44.4	0.47	−0.48	0.95
TMPD	2.192	613	43.6	−0.79	44.4	0.47	−0.48	0.95
pyridine	2.213	572	41.1	−0.79	41.9	0.45	−0.48	0.93

[a] Sign of the coupling constants is taken to be positive according to Brown and Hoffman [10].

ligand π orbitals may be expected to make some important role, but the observed trends in the present work indicate that the direct interaction of the d orbitals with the π donors or acceptors makes important contributions to the perturbation of the metal d orbital states.

The X-ray analysis for crystals of CT complexes of ZnTPP, MnTPP, and CrTPP with toluene shows that the ortho carbon of toluene, the most electron rich positions, situates above the metal ions in the crystals [1(i,j)], and it seems to be suggestive that the direct interaction between the metal d orbitals and the donor or acceptor molecules plays some important role in the CT complex formation.

CT Complexes of Copper(II) Porphyrins

Tables III and IV list the obtained EPR and ENDOR parameters. As the changes of $g_\perp$ and $A_\perp^{Cu}$ values by the complex formation are much smaller than those of $g_\parallel$ and $A_\parallel^{Cu}$ values, and their accurate determination is difficult, the $g_\perp$ and $A_\perp^{Cu}$ values are not listed in the Tables. The $A_\perp^N$ and $A_\perp^H$ values were determined from the ENDOR spectra which were observed by setting the magnetic field at the lowest field component of $g_\parallel$ in the EPR spectra [11]. In the ENDOR measurements two kinds of proton signals were observed for CuOEP and CuTPP, but Tables III and IV list only the data with larger hf coupling constants, which may be assigned to the interaction with the meso protons for CuOEP and to that with the pyrole ring protons for CuTPP, respectively.

The observed ligand hf coupling constants contain contribution from the spins localized on copper, A_d^N and A_d^H, and from the spins delocalized on the ligand, A_i^N and A_i^H.

As the former are evaluated by the equations,

$$A_d^N = -(\rho/h)g\beta g_N\beta_N\left(1+\frac{9}{7}\frac{\langle r^2\rangle}{R}\right)R_N^{-3} \qquad (5)$$

for nitrogen nuclei, and for protons

$$A_d^H = -(\rho/h)g\beta g_H\beta_H R_H^{-3}, \qquad (6)$$

the latter can be estimated by substracting A_d^N or A_d^H from the observed coupling constants $A_\perp^N$ or $A_\perp^H$, respectively. In the equations 5 and 6, ρ is the spin density on the copper ion and is evaluated from the EPR spectra [12], R_N and R_H are the distances from the copper ion to the nitrogen nuclei and to the protons and $\langle r^2\rangle = \langle d_{xy}|r^2|d_{xy}\rangle$, respectively. In the present calculation, R_N, R_H(pyrole protons), R_H (meso protons) and $\langle r^2\rangle$ were taken to be 1.98 Å, 524 Å, 4.52 Å [13], and 3/4 Å^2 [14], respectively.

As Tables III and IV show, the effects of the complex formation with π donors or acceptors are small in the copper porphyrins, but they are not negligible. As in the case of the cobalt porphyrins, the effects for the OEP complexes are larger than those for the TPP complexes. The $g_\parallel$ values of the copper porphyrins decrease while the $A_\parallel{}^{Cu}$ values increase by the interaction with the stronger π acceptors.

According to the equation [15],

$$g_\parallel = g_e - \frac{8\xi\alpha^2}{\Delta E(B_{2g})} \qquad (7)$$

where ξ and α^2 ($=\rho$) are spin orbit coupling and bonding parameters, respectively, the decrease of the $g_\parallel$ value can be attributed to the increase of $\Delta E(B_{2g})$, corresponding to elevation of the $3d_{xy}$ level, and to the increase of covalency in the Cu–N σ bonds [15]. The changes in the covalency in the Cu–N σ bonds can also be seen by the changes of the ligand hf coupling constants $A_i{}^N$ and $A_i{}^H$. The CT from the copper d orbitals to the π acceptors will induce increases of the σ electron donation from the porphyrin ligand to the copper ion, leading to elevation of the copper $3d_{xy}$ level as well as increase of covalency in the copper–porphyrin bonds. The reverse can be considered for the interaction with π donors. Electrostatic fields from the donor, acceptor or solvent molecules may have some effects on the changes of the d orbital levels as was seen for the cobalt porphyrins. However, it should be emphasized that in the interaction of the copper porphyrins with π donors or acceptors the direct CT between the copper d orbitals and the donors or acceptors makes an important contribution to the perturbation of the copper electronic states as in the case of the cobalt porphyrins.

References

1 (a) M. Gouterman and P. E. Stevenson, *J. Chem. Phys.*, *37*, 2266 (1962);
(b) J. G. Heathcoat, G. J. Hill, P. Rothwell and M. A. Slifkin, *Biochem. Biophys. Acta*, *153*, 13 (1968);
(c) C. D. Barry, H. A. O. Hill, B. E. Mann, P, J. Sadler and R. J. P. Williams, *J. Am. Chem. Soc.*, *95*, 4545 (1973);
(d) H. A. O. Hill, P. J. Sadler and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, 1663 (1973);
(e) H. A. O. Hill, B. E. Mann and R. J. P. Williams, *J. Chem. Soc., Chem. Commun.*, *905*, 906 (1967);
(f) H. A. O. Hill, A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc., A*, 1704 (1969);
(g) C. D. Barry, H. A. O. Hill, P. J. Sadler and R. J. P. Williams, *Proc. R. Soc. London, Ser. A*, *334*, 493 (1973);
(h) G. P. Fulton and G. N. La Mar, *J. Am. Chem. Soc.*, *98*, 2119, 2124 (1976);
(i) W. R. Scheidt, M. E. Kastner and K. Hatano, *Inorg. Chem.*, *17*, 706 (1978);
(j) W. R. Scheidt and C. A. Reed, *Inorg. Chem.*, *17*, 710 (1978);
(k) H. Yokoi and M. Iwaizumi, *Bull. Chem. Soc. Jpn.*, *53*, 1489 (1980).
2 F. A. Walker, *J. Magn. Reson.*, *15*, 201 (1974).
3 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, *32*, 2443 (1970).
4 (a) W. R. Scheidt, *Acc. Chem. Res.*, *10*, 339 (1977);
(b) E. B. Fleischer, G. K. Miller and L. E. Webb, *J. Am. Chem. Soc.*, *86*, 2342 (1964).
5 W. C. Lin, *Mol. Phys.*, *31*, 657 (1976).
6 The x and y axes are taken to bisect the N–metal–N angle.
7 W. C. Lin, *Inorg. Chem.*, *15*, 1114 (1976).
8 M. A. Hitchman, *Inorg. Chem.*, *16*, 1985 (1977).
9 (a) M. J. Hamor, T. A. Hamor and J. L. Hoard, *J. Am. Chem. Soc.*, *86*, 1938 (1964);
(b) E. B. Fleischer, C. K. Miller and L. E. Webb, *J. Am. Chem. Soc.*, *86*, 2342 (1964);
(c) D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, *96*, 2095 (1974).
10 T. G. Brown and B. M. Hoffman, *Mol. Phys.*, *39*, 1073 (1980).
11 G. H. Rist and J. S. Hyde, *J. Chem. Phys.*, *52*, 4633 (1970).
12 D. Kivelson and R. Neiman, *J. Chem. Phys.*, *35*, 149 (1961).
13 D. A. Case and M. Karplus, *J. Am. Chem. Soc.*, *99*, 6182 (1977).
14 G. H. Rist and J. S. Hyde, *J. Chem. Phys.*, *50*, 4532 (1969).
15 (a) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, *29*, 31, 35 (1958);
(b) B. R. McGarvey, 'Transition Metal Chemistry', ed. by Carlin; Marcel Dekker, Inc.: New York, 3, 89 (1967).