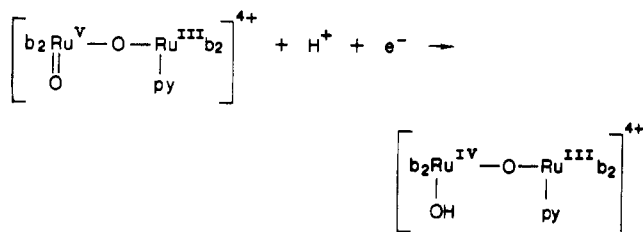mixed-ligand ion, the relevant couple is 1-electron in character (Figure 3)
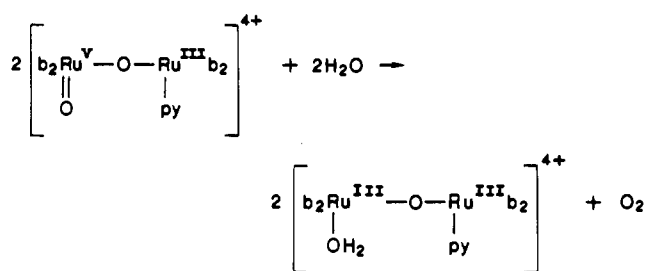
$$\left[\begin{array}{c} b_2Ru^V - O - Ru^{III}b_2 \\ \parallel \qquad\quad | \\ O \qquad\quad py \end{array}\right]^{4+} + H^+ + e^- \longrightarrow$$

$$\left[\begin{array}{c} b_2Ru^{IV} - O - Ru^{III}b_2 \\ | \qquad\qquad | \\ OH \qquad\quad py \end{array}\right]^{4+}$$

and for the diaqua dimer, it is 3-electron in character[2c]

$$\left[\begin{array}{c} b_2Ru^V - O - Ru^Vb_2 \\ \parallel \qquad\quad \parallel \\ O \qquad\quad O \end{array}\right]^{4+} + 3H^+ + 3e^- \longrightarrow$$

$$\left[\begin{array}{c} b_2Ru^{IV} - O - Ru^{III}b_2 \\ | \qquad\qquad | \\ OH \qquad\quad OH_2 \end{array}\right]^{4+}$$
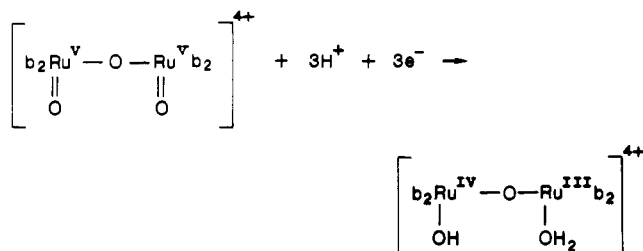
When fully oxidized, the diaqua ion has the thermodynamic capability of direct 4-electron oxidation of H_2O to O_2

$$\left[\begin{array}{c} b_2Ru^V - O - Ru^Vb_2 \\ \parallel \qquad\quad \parallel \\ O \qquad\quad O \end{array}\right]^{4+} + 2H_2O \longrightarrow O_2 +$$

$$\left[\begin{array}{c} b_2Ru^{III} - O - Ru^{III}b_2 \\ | \qquad\qquad | \\ OH_2 \qquad\quad OH_2 \end{array}\right]^{4+}$$

$$E^{O'} = 0.28 \text{ V at pH} = 1^{2c}$$
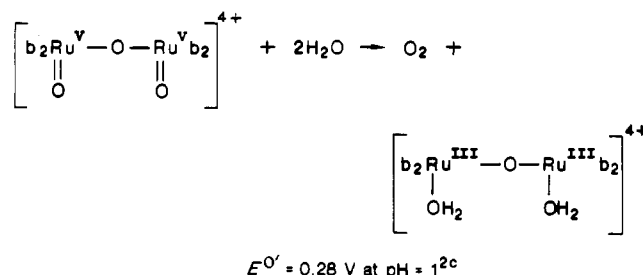
The mixed-ligand dimer is also thermodynamically capable of H_2O oxidation but on the basis of a 2-equiv demand

$$2\left[\begin{array}{c} b_2Ru^V - O - Ru^{III}b_2 \\ \parallel \qquad\quad | \\ O \qquad\quad py \end{array}\right]^{4+} + 2H_2O \longrightarrow$$

$$2\left[\begin{array}{c} b_2Ru^{III} - O - Ru^{III}b_2 \\ | \qquad\qquad | \\ OH_2 \qquad\quad py \end{array}\right]^{4+} + O_2$$

Nonetheless, even the implied ability of the mixed-ligand dimer to oxidize H_2O to O_2 is a significant observation since it suggests that if sufficiently oxidizing, mechanistic pathways may exist which allow a *single* metal site to act as a catalyst for the oxidation of H_2O to O_2.

Ligand Field Effects in the Nuclear Magnetic Shielding of Nitrogen-15 and Cobalt-59 in Bent Nitrosyl Complexes of Cobalt(III)

Paul A. Duffin,[1] Leslie F. Larkworthy,*[1] Joan Mason,*[2] Alan N. Stephens,[1] and Russell M. Thompson[1]

Received August 29, 1986

A range of square-pyramidal complexes of cobalt(III) with a bent apical nitrosyl ligand has been prepared and examined by ¹⁵N and ⁵⁹Co NMR spectroscopy, in a study of nephelauxetic and spectrochemical effects at the metal and nitrogen nuclei in the bent Co–NO chromophore. The basal ligands in this comparison include dithiocarbamate, quadridentate Schiff base or porphine, and bis-chelating diamine or oximate, so as to give S₄, S₂N₂, N₄, OONN, or ONON coordination in the plane and a range of substituents in the chelate and phenylene rings. The shielding of both cobalt and nitrogen tends to decrease with decrease in the M(d) → π*(NO) back-bonding, as indicated by the MN and NO bond distances, the MNO angle and the NO stretching frequency. The shieldings decrease from sulfur to nitrogen to oxygen coligators and also with electron withdrawal by ring substituents (and vice versa), i.e. with decrease in the ligand field splitting and in the nephelauxetism of the coligands. These parallelisms of the cobalt and nitrogen shielding accord with the orbital theory that was developed to explain the bending of the MNO ligand and influences of the metal and coligands. Significant interdependence of spectrochemical and nephelauxetic effects at cobalt and nitrogen arises from the degree of overlap and similarity in energies of the frontier orbitals for the paramagnetic circulation at nitrogen [n(N) → π*(NO)] and at cobalt (d–d).

Introduction

¹⁵N NMR spectroscopy is a sensitive indicator of the nature of the nitrosyl ligand, whether linear,[3,4] strongly bent with MNO

angle 120–130°,[5–8] partially bent (as e.g. in dinitrosyls),[9] or bridging.[10] In terminal nitrosyls the nitrogen shielding decreases

(1) University of Surrey.
(2) The Open University.
(3) Botto, R. E.; Kolthammer, B. W. S.; Legzdins, P.; Roberts, J. D. *Inorg. Chem.* **1979,** *18,* 2049.
(4) Butler, A. R.; Glidewell, C.; Hyde, A. R.; McGinnis, J. *Inorg. Chem.* **1985,** *24,* 2931.
(5) Bell, L. K.; Larkworthy, L. F.; Mason, J.; Mingos, D. M. P.; Povey, D. C.; Sandell, B. *J. Chem. Soc., Chem. Commun.* **1983,** 125.
(6) Bell, L. K.; Mason, J.; Mingos, D. M. P.; Tew, D. G. *Inorg. Chem.* **1983,** *22,* 3497.

Chart I
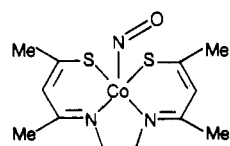
1, [Co(NO)(sacacen)]
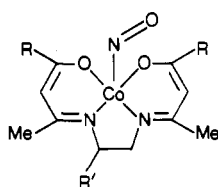
2a, [Co(NO)(acacen)]; R = Me, R′ = H
b, [Co(NO)(acacpn)]; R = R′ = Me
c, [Co(NO)(benacen)]; R = Ph, R′ = H
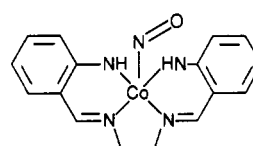
3, [Co(NO)(amben)]

4a, [Co(NO)(salen)]; R = R′ = H
b, [Co(NO)(5-*t*-Busalen)]; R = 5-*t*-Bu, R′ = H
c, [Co(NO)(3,5-(NO₂)₂salen)]; R = 3,5-(NO₂)₂, R′ = H
d, [Co(NO)(7-Mesalen)]; R = H, R′ = Me

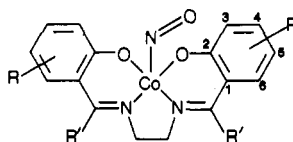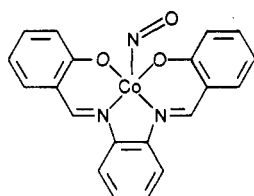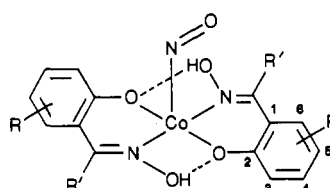5, [Co(NO)(salphen)]

6a, [Co(NO)(salox)₂]; R = R′ = H
b, [Co(NO)(3-MeOsalox)₂]; R = 3-OMe, R′ = H
c, [Co(NO)(5-Clsalox)₂]; R = 5-Cl, R′ = H
d, [Co(NO)(5-NO₂salox)₂]; R = 5-NO₂, R′ = H
e, [Co(NO)(ketox)₂]; R = H, R′ = Me

(the shift increases) as the MNO angle decreases. The strong deshielding in the strongly bent (MNO)[8] nitrosyls of the present study resembles that in main-group nitroso (R–NO) or nitrosyl (NOX) compounds, which arises from low-energy n(N) → π*-(NO) paramagnetic circulations (magnetic dipole allowed excitations).[11] These are made possible in metal nitrosyls by the development of a lone pair on the nitrogen as the nitrosyl bends, and the strongly bent ligand is usefully viewed as NO⁻ attached to (low-spin) cobalt(III).

The ability of the NO ligand to bend, in contrast to related ligands such as CO or N₂, was explained in terms of the similarity of the energies of the HOMO and LUMO at nitrogen, the n(N) and (π*NO) orbitals, to those of the ligand field orbitals.[12-14] Thus the shielding theory that suggested the strong dependence of the nitrogen shift on the degree of MNO bending also suggests a link between the nitrogen shift and that of the transition-metal nucleus. An objective of our investigation has been to explore this connection. The shielding of the metal nucleus depends on d–d paramagnetic circulations,[15] which are sensitive (particularly with relatively weak ligands, as in the present study) to the ligand field splittings, which are modified by the interaction with the frontier orbitals of the nitrosyl which mediate the nitrogen shifts. Such a connection has more than theoretical interest since the reactivity, indeed lability, of the bent nitrosyl ligand is bound up with the ease of internal M(dπ) ↔ NO (n) redox processes as involved in the bending.[14,16,17] The "lone pair" on nitrogen is in fact a loose term for electron density in the MNO plane, which is high lying (avoids the σ bonds) and also delocalized in d orbitals in the MNO plane, as discussed below, while the π*(NO) orbitals are good π-acceptors. Overall, shift of d-electron density onto nitrogen with bending of MNO predisposes the metal to reaction with nucleophiles, and the nitrosyl to reaction with electrophiles.

Thus the combination of ¹⁵N and ⁵⁹Co NMR is particularly suitable as a probe of these orbital interactions. The remarkable range of over 850 ppm in ¹⁵N shift in cobalt nitrosyl complexes, depending on the MNO angle, may be linked to the equally remarkable range of ⁵⁹Co shifts, over 19 000 ppm in toto, the largest range for spin-paired compounds of any nucleus. The square-pyramidal complexes of cobalt with bent apical nitrosyls are appropriate to this study, for two reasons. First, although five-coordinate, none show any signs of fluxionality, as observed in five-coordinate nitrosyl complexes with monodentate coligands and associated with an alternative trigonal-bipyramidal structure.[8] The spectroscopic evidence confirms that the square-pyramidal structure is maintained in solution in each case. The quadridentate Schiff base ligands have little flexibility when coordinated, the ketox and salox nitrosyls also are kept as square pyramids by strong hydrogen bonds among the basal ligands,[7] and the complexes with bidentate ligands, such as dithiocarbamate, follow suit. Second, there is considerable scope for variation of the basal quadridentate or bis-chelate ligands (cf, **1–6**; see (Chart I) whether Schiff base,[18,20,21] porphine, oxime,[19] diamine, dithiocarbamate, etc. A

(7) Bultitude, J.; Larkworthy, L. F.; Mason, J.; Povey, D. C.; Sandell, B. *Inorg. Chem.* **1984**, *23*, 3629 and references therein.
(8) Mason, J.; Mingos, D. M. P.; Schaefer, J.; Sherman, D.; Stejskal, E. O. *J. Chem. Soc., Chem. Commun.* **1985**, 444. Mason, J.; Mingos, D. M. P. Sherman, D.; Wardle, R. W. M. *Ibid.* **1984**, 1223.
(9) Evans, D. H.; Mason, J.; Mingos, D. M. P.; Richards, A.; *J. Organomet. Chem.* **1983**, *249*, 293.
(10) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034. Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.
(11) Mason, J. *Chem. Rev.* **1981**, *81*, 205. Mason, J., Ed. *Multinuclear NMR*; Plenum: New York, 1987; Chapter 12.
(12) Mingos, D. M. P. *Inorg. Chem.* **1973**, *12*, 1209.
(13) Hoffmann, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666.
(14) Eisenberg, R.; Meyer, C. *Acc. Chem. Res.* **1975**, *8*, 26.
(15) (a) Mason, J. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 199; **1976**, *18*, 197. Mason, J. *Chem. Rev.*, in press. (b) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed., Plenum: New York, 1987; Chapter 3.

(16) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.
(17) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. Feltham, R. D.; Enemark, J. E. *Top. Stereochem.* **1981**, *12*, 155.
(18) Earnshaw, A.; Hewlett, P. C.; Larkworthy, L. F. *J. Chem. Soc.* **1965**, 4718.
(19) Varothai, O. Ph.D. Thesis, University of Surrey, 1969.

useful range of ligand field relationships may be obtained by changes in the coligators from sulfur to nitrogen or oxygen, and also by varying the nature and substitution of the chelate and phenylene rings. We have synthesized some new nitrosyls to this end, including one with an N_4-ligating Schiff base, [Co(NO)-(amben)] (**3**).

A further incentive has been that the distinctive position of the resonances makes ^{15}N NMR spectroscopy a useful method of investigation of the redox reactions of the bent nitrosyls, some of which are evident in the NMR spectra, particularly with long acquisition times. The [59]Co shifts and line widths provide a useful check on the nature of the species in solution, the dispersion of the shifts making up for the breadth of the lines. The bent nitrosyls of cobalt can function as oxygen-transfer agents, via a nitrosyl-nitro couple;[20,21] and oxidation of the related myoglobin nitrosyl (in cured meats) is of importance to the food industry. The nitro ligand[22] resembles the bent nitrosyl in its lability: linkage isomerism, ligand exchange, and reduction of Co(III) to Co(II) with loss of the NMR spectrum have been observed.

Experimental Section

To maximize sensitivity, the ^{15}N spectra were measured with 99% ^{15}N-enrichment of the nitrosyl, on a 400-MHz spectrometer. Infrared spectra of Nujol mulls, KBr disks, or solutions of the [14]NO and [15]NO complexes were recorded over the range 4000–400 cm^{-1}.

The sacacenH$_2$ ligand N,N'-ethylenebis(monothioacetylacetone imine) was prepared as before[23] from acacenH$_2$, N,N'-ethylenebis(acetylacetone imine). The salenH$_2$, salphenH$_2$, 7-MesalenH$_2$, 5-NO$_2$salenH$_2$, and 3,5-(NO$_2$)$_2$salenH$_2$ ligands were obtained by condensation of the appropriate aldehyde and amine by standard methods. 3,5-Dinitrosalicylaldehyde was prepared by nitration of salicylaldehyde, and the other aldehydes and 2-hydroxyacetophenone were obtained commercially.

The oximes were prepared by reaction of hydroxylamine hydrochloride with salicylaldehyde or 5-chlorosalicylaldehyde.

The ambenH$_2$ ligand, N,N'-ethylenebis(2-aminobenzylideneamine),[24] was made by the reduction of 2-nitrobenzaldehyde to 2-aminobenzaldehyde with iron(II) sulfate in concentrated ammonia, followed by condensation with ethylenediamine. *meso*-Tetraphenylporphine (TPP) was made by standard methods.[25,26]

[14]NO was generated from sodium nitrite and acidified iron(II) sulfate. [15]NO (99%) was supplied by Prochem Ltd. Solvents were carefully dried and deoxygenated, and the nitrosyls were prepared as before[18,19] except for minor variations in procedure indicated below.

Preparation of [15]NO-Labeled Complexes. The salen derivatives were prepared as before,[7] hydrated cobalt(II) acetate being mixed with the ligand under [15]NO with solvents as specified: [Co([15]NO){3,5-(NO$_2$)$_2$salen}], DMF to which water was added after reaction; [Co-([15]NO)(5-t-Busalen)] and [Co([15]NO)(salphen)],[21] DMF; [Co([15]NO)(7-Mesalen)], methanol. The oximato complexes [Co([15]NO)(5-NO$_2$salox)$_2$] and [Co([15]NO)(5-Clsalox)$_2$] were similarly isolated from methanol, as were [Co([15]NO)(sacacen)][20] and [Co([15]NO)(acacpn)]. The last complex is very soluble, and it was necessary to take the solvent to dryness. The unlabeled compound was obtained by the addition of water to the methanol solution and analyzed as a monohydrate.

To prepare [Co([15]NO)(amben)] the [15]NO was admitted to a flask containing a well-stirred suspension of [Co(amben)][24] in toluene. [Co-([15]NO)(TPP)] was similarly prepared from a solution of [Co(TPP)][27] in CH$_2$Cl$_2$ containing some piperidine. It was crystallized by the addition of methanol to the boiling solution, followed by slow cooling. The perchlorate [Co([15]NO)(en)$_2$(OClO$_3$)](ClO$_4$) was prepared by the mixing of cobalt(II) perchlorate with ethylenediamine in methanol under [15]NO.[28]

The unlabeled complexes were prepared in an excess of nitric oxide, about 1 mol of the gas being absorbed per mol of cobalt(II). Satisfactory

analyses were obtained for all the nitrosyls; the data for new compounds are given in Table II.

Results and Discussion

Spectroscopic Measurements. Table I gives NMR and IR spectroscopic measurements for the square-pyramidal complexes with bent apical nitrosyl and chelating basal coligands. Structural data are included for comparison, so far as these are known, i.e., for the bis(dithiocarbamate),[29,30] bis(ethylenediamine),[31] TPP,[32] acacen and benacen,[33] salen,[34] 7-Mesalen,[35a] and bis(ketox), -(salox), and -(5-Clsalox)[35b] nitrosyls.

The NMR and IR spectroscopic evidence confirms that the square-pyramidal structure observed in the solid state persists in solution. Work in progress with solid-state ^{15}N NMR[36] has shown relatively small differences in nitrogen shift from the solution values: the isotropic shift for [Co([15]NO)(7-Mesalen)] is 719 ppm as compared with 710 ppm in CH$_2$Cl$_2$ solution. As mentioned above, none of the spectra show signs of fluxionality. The IR spectra are very rich, and there is a high degree of correspondence of the [Co(NO)(L$_4$] spectrum (except for the band representing the NO stretching vibration) with that of the parent near-planar complex, whether in the solution or in the solid phase. Each of the complexes studied was made with [14]NO and with [15]NO, but the only significant spectral differences were those of the NO stretching frequencies, because of the abundance of the basal ligand vibrations.

Two nitrosyl resonances differing in intensity were observed for certain of the compounds, showing the presence of distinct species. In the solution of [Co(NO)(en)$_2$](ClO$_4$)$_2$ these might be complexes with either acetone or perchlorate at the otherwise vacant site. In the solid state a perchlorate ligand was found, trans to the nitrosyl, and supported by extensive hydrogen-bonding to the NH$_2$ groups.[31] The cobalt spectrum shows an additional weaker line at higher frequencies, as expected for an O-bonded ligand. In [Co(NO)(amben)] (**3**) three isomers are possible in principle, depending on the orientations of the nitrosyl and the two N–H groups. If both N–H groups project from the same side of the [Co(amben)] plane the attack of NO from the other side is presumably favored. In the cobalt spectrum, however, the additional weaker line is much sharper. In [Co(NO)(acacpn)] (**2b**) the nitrosyl and the methyl group may project from the same side or from opposite sides of the Co(acacpn) plane, and the latter may be favored. The ligand is dissymmetric, so that R and S forms are possible.

An interesting example of solid-state effects related to flexibility in the basal ligand is afforded by [Co(NO)(salen)] and its derivatives. The solid-state structure of [Co(NO)(salen)][34] contains two independent molecules that differ in their salen conformations and NO distances (1.071 and 1.163 Å), although the M–N distances are the same within the experimental uncertainty (mean values are given in Table I). The conformation in [Co(NO)(7-Mesalen)][35a] resembles the umbrella conformer in the [Co-(NO)(salen)] structure, in which the two planes containing the phenylene groups are angled away from the nitrosyl, at a few degrees to the CoOONN plane; in the other (stepped) conformer of [Co(NO)(salen)] one of the phenylene planes is angled toward the nitrosyl and one is angled away from the nitrosyl.[34] The two

(20) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528.
(21) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1981**, *101*, 270. Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A. *J. Am. Chem. Soc.* **1981**, *103*, 3522.
(22) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55.
(23) Blum, P. R.; Wei, R. M. C.; Cummings, S. C.; *Inorg. Chem.* **1974**, *13*, 450.
(24) Green, M.; Tasker, P. A. *J. Chem. Soc. A* **1970**, 3105.
(25) Adler, A. D.; Longo, F. R.; Finavelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *31*, 476.
(26) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1401.
(27) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
(28) Ileperuma, O. A.; Feltham, R. D. *Inorg. Synth.* **1976**, *16*, 5.

(29) Enemark, J. H.; Feltham, R. D. *J. Chem. Soc., Dalton Trans.* **1972**, 718.
(30) Brewer, G. A.; Butcher, R. J.; Letafat, B.; Sinn, E.; *Inorg. Chem.* **1983**, *22*, 371.
(31) Johnson, P. L.; Enemark, J. H.; Feltham. R. D.; Swedo, K. B. *Inorg. Chem.* **1976**, *15*, 2989.
(32) Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8281.
(33) Wiest, R.; Weiss, R. *Rev. Chim. Miner.* **1972**, *9*, 655.
(34) Haller, K. J.; Enemark, J. H. *Acta Crystallogr. Sect. B: Crystallogr. Cryst. Chem.* **1978**, *B34*, 102.
(35) (a) Larkworthy, L. F.; Povey, D. C.; Smith, G. T.; Tucker, B. J., submitted for publication. (b) Larkworthy, L. F.; Povey, D. C. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 413. Gallagher, M.; Ladd, M. S. C.; Larkworthy, L. F.; Povey, D. C.; Salib, K. A. R. *Ibid.* **1986**, *16*, 967.
(36) unpublished work with C. Brévard.

Table I. Spectroscopic and Structural Data for Square-Pyramidal Cobalt(III) Complexes with a Bent Apical Nitrosyl[a]

compd	$\delta(^{15}N)$	MNO/deg	NO/Å	MN/Å	$\nu(^{14}NO)/cm^{-1}$	$\delta(^{59}Co)$	$W_{1/2}/Hz$
		S₄ Coligands					
$[Co(^{15}NO)(S_2CNR_2)_2]^k$							
R = Me[c]	501.3	135.1	1.17	1.75	1625	6668	750
R = Me[d]	502.6					6906	2150
R = Et[c]	500.8				1625	6642	1150
					1660[f,h]		
R = i-Pr[b]	526.9	129.2	1.11	1.71	1637		
		S₂N₂ Coligand					
$[Co(^{15}NO)(sacacen)]^d$ **(1)**	672.1				1638	7164[d]	6400
		N₄ Coligands					
trans-$[Co(^{15}NO)(en)_2](ClO_4)_2^e$	717.5	(disordered)		1.806	1663	7357[e]	2100
	727.6 less strong					7612 vw	2600
$[Co(^{15}NO)(amben)]^b$ **(3)**	734.3				1630	6559[b]	4800
	698.5 w					6687 w	550
$[Co(^{15}NO)(TPP)]^{b,j}$	770.7	(disordered)		1.833	1690[g]	7909[b]	4250
		OONN (acen) Coligands					
$[Co(^{15}NO)(acacpn)]^b$ **(2b)**	711.5				1650		
	726.7 w						
$[Co(^{15}NO)(acacen)]^k$ **(2a)**	714.3[d]	122.4	1.093	1.821	1654	8001[c]	1700
					1650[b,i]		
					1655[c]		
$[Co(^{15}NO)(benacen)]^k$ **(2c)**	723.0[d]	122.9	1.136	1.831	1630[d]	8170[b]	2550
	726.8[c]				1653[b,i]	7449[c]	5800
	724.7[b]				1635		
		OONN (salen) Coligands					
$[Co(^{15}NO)(7-Mesalen)]^b$ **(4d)**	710.0	127.4	1.131	1.793	1615	9100[b]	2250
$[Co(^{15}NO)(5-t-Busalen)]^b$ **(4b)**	721.9				1630		
$[Co(^{15}NO)(salen)]^k$ **(4a)**	725.4[b]	127.0	1.117	1.807	1624	7658[c]	11 700
	736.9[d]				1626[d]	8100[d]	
					1666[b,i]		
$[Co(^{15}NO)(salphen)]^d$ **(5)**	769.7				1660	9300[d]	5700
					1630		
$[Co(^{15}NO)\{3,5-(NO_2)_2salen\}]^d$ **(4c)**	820.5				1725	not obsd	
		ONON Coligands					
$[Co(^{15}NO)(ketox)_2]^k$ **(6e)**	740.3[c,l]	126.3	1.114	1.806	1675	8478[c,m]	240
	741.1[b,n]				1635[d]	9390[d]	4000
$[Co(^{15}NO)(3-MeOsalox)_2]$ **(6b)**	756.6[b,n]				1667[g]	9623[b]	2600
	817.0[d]					8446[d]	16800
$[Co(^{15}NO)(salox)_2]^{d,k}$ **(6a)**	824.1[n]	(disordered)		1.838	1672	8586[c]	3000
						8966[d]	2700
$[Co(^{15}NO)(5-Clsalox)_2]^d$ **(6c)**	828.7[n]	123.4	1.070	1.841	1690[g]	9890[d]	9000
$[Co(^{15}NO)(5-NO_2salox)_2]^d$ **(6d)**	833.1[n]				1705		

[a] $\delta(^{15}N)$ relative to neat liquid nitromethane and $\delta(^{59}Co)$ relative to aqueous $K_3[Co(CN)_6]$, high frequency positive; br signifies a broad resonance (ca. 20 Hz), w a weak (vw, very weak) additional resonance. $W_{1/2}$ is the ^{59}Co line width at half-height, not optimized. Measured at 25 °C in deuterated solvents *b–e*. References for the structural data are given in the text. IR stretching frequencies were measured on the Nujol mull, unless otherwise indicated. The frequencies are about 30 cm^{-1} lower in the ^{15}N compounds. [b] CH_2Cl_2. [c] $CHCl_3$. [d] Me_2SO. [e] Acetone. [f] CCl_4. [g] KBr disk. [h] Carlin, R. L.; Canziani, F.; Bratton, W. K. *J. Inorg. Nucl. Chem.* **1964**, *25*, 898. [i] Reference 37. [j] TPP is *meso*-tetraphenylporphine. [k] Reference 7. [l] Partially resolved octet, $^1J(Co^{15}N) \simeq 9$ Hz. [m] Septet, $^4J(CoH) = 540$ Hz. [n] Broadened by unresolved coupling to ^{59}Co.

Table II. Analytical Data for the New Nitrosyl Complexes

	anal. found (calcd)			
compd	% C	% H	% N	% Co
$[Co(NO)(amben)]$	54.4 (54.4)	4.4 (4.6)	20.0 (19.8)	16.6 (16.7)
$[Co(NO)(acacpn)]\cdot H_2O$	45.9 (45.5)	5.9 (6.5)	12.2 (12.2)	
$[Co(NO)(7-Mesalen)]$	56.2 (56.4)	4.6 (5.3)	10.6 (11.0)	
$[Co(NO)(5-t-Busalen)]$	61.5 (61.7)	6.6 (6.4)	9.0 (9.0)	12.6 (12.6)
$[Co(NO)\{3,5-(NO_2)_2salen\}]$	36.8 (35.9)	1.7 (1.9)	18.1 (18.3)	
$[Co(NO)(5-Clsalox)_2]$	39.5 (39.1)	2.4 (2.3)	9.1 (9.8)	
$[Co(NO)(5-NO_2salox)_2]$	36.8 (37.4)	2.9 (1.8)	14.8 (15.6)	13.4 (13.1)

NO stretching frequencies given for the salphen compound in Table I, similarly, suggest two NO environments in the solid, and doubling of the ^{15}N peaks is observed in the solid-state NMR spectrum.[36]

Various solvent effects are possible, such as loose association of a solvent molecule trans to the nitrosyl when a coordinating solvent such as Me_2SO or acetone is used, as may be necessary to get the complex into solution. Only small changes in the electronic spectrum, however, were reported on addition of nitrogen or phosphorus bases to solutions of the bent nitrosyls.[20] It has also been suggested that increased polarity of the solvent may

influence the MNO angle by favoring a more polar form of the nitrosyl.[37]

The magnitude of such effects can be seen by examination of Table I. As to the complexes with bidentate ligands, which might show greater flexibility, effectively the same nitrogen shift is observed for $[Co(^{15}NO)(S_2CNMe_2)_2]$ in chloroform or Me_2SO solvent, and the difference in nitrogen shift is only 10 ppm for the two peaks given by $[Co(^{15}NO)(en)_2]^{2+}$ which may represent

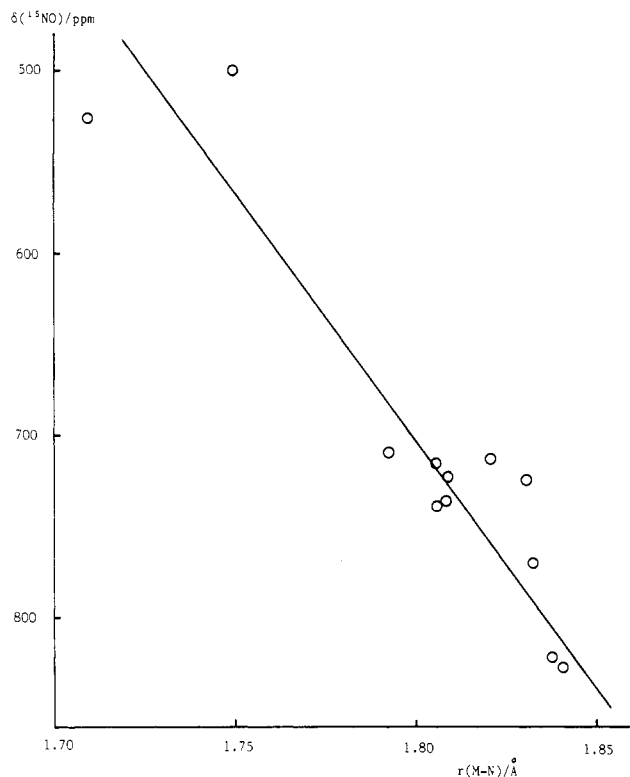(37) Tamaki, M.; Masuda, I.; Shinra, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 171.

Figure 1. Correlation of the nitrogen shift with the CoN bond distance in the bent nitrosyl ligand.

Figure 2. Correlation of the nitrogen shift with the NO stretching frequency in the bent nitrosyl ligand.

association with acetone or perchlorate. Change from a chlorinated solvent to Me_2SO makes little difference in the nitrogen shifts of the benacen and salen nitrosyls (**2c** and **4a**), although a larger change, of 50 ppm, is observed for $[Co(^{15}NO)(3\text{-MeO-salox})_2]$ (**6b**).

Changes of a few wavenumbers in the NO stretching frequency, or 20 cm^{-1} at most, are observed from the solid state to solution in $CHCl_3$, CH_2Cl_2, or Me_2SO for the acen complexes. Certain compounds show larger solvent effects: in the salen complex (**4a**) this frequency is 40 cm^{-1} less in Me_2SO or a Nujol mull than in CH_2Cl_2, and in the ketox complex (**6e**) the frequency is 40 cm^{-1} less in Me_2SO than in a Nujol mull (so these differences are not systematic). In the ketox compound, however, the ^{15}N shielding is reduced by 40 ppm in the solid state compared to that in the solution.[36] There may be a tendency for medium effects to increase with deshielding of the nitrogen, perhaps because small changes have a greater proportionate effect when excitation energies are small.

Correlation of the Nitrogen Shielding with MNO Structure. Figure 1 shows that there is a tendency for the nitrogen shielding to increase with decrease in the M—NO bond distance. This bond length reflects back-bonding in the M—N≡O ligand, which is very strong for linear nitrosyls and less strong but still important in the bent ligand, as will be discussed. The M–NO distances, 1.7–1.85 Å in Table I, are reduced compared with MN bond lengths of 1.9–2.0 Å in the chelating ligands, and values near 2.0 Å in ammine or amine complexes in general.

Figure 2 shows the related trend for the nitrogen shielding to increase with decrease in the NO stretching frequency, and concomitant trends of increase in NO bond length and MNO angle are evident in Table I. These correlations are expected to be poorer than that with the M–N bond length because of the sensitivity of the geometry of the projecting nitrosyl to crystal forces and solvent interactions. As mentioned, these solvent effects are mostly small, but for certain compounds may be as large as 40 cm^{-1}.

Correlation of the Nitrogen and Cobalt Shifts. Figure 3 tests the prediction of a tendency for the nitrogen and cobalt shielding to increase together, both increasing with increase in the back-bonding. The connection between these three is an intricate one, and a good correlation is not to be expected, as independent
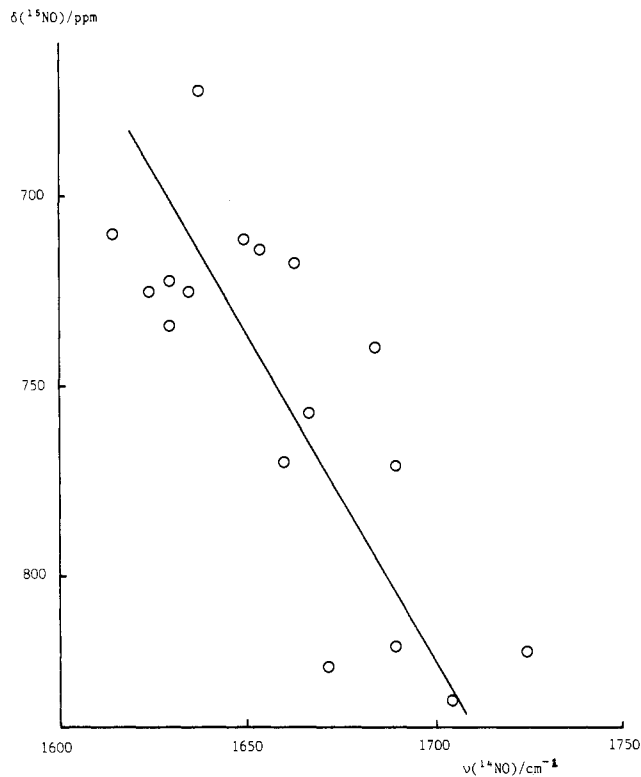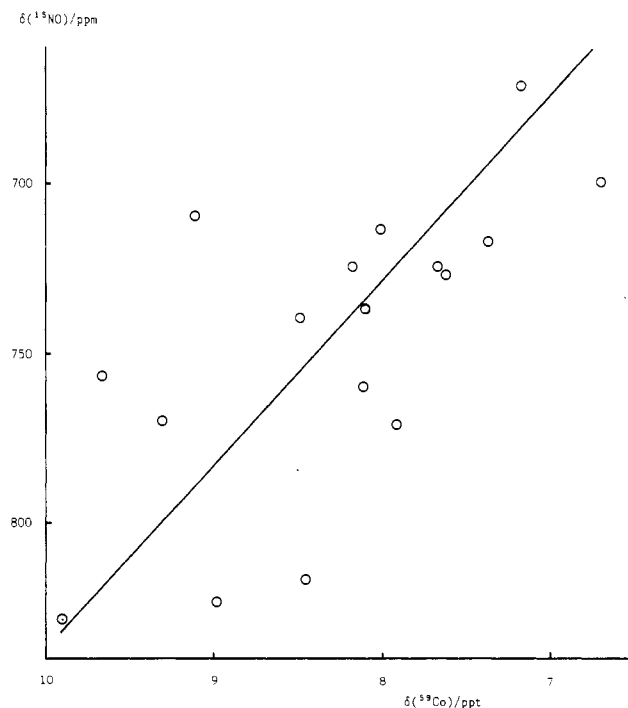

Figure 3. Correlation of the nitrogen and cobalt shifts in the bent nitrosyl ligand.

influences on the cobalt and nitrogen shielding are present also. The trend is discernible, with considerable scatter, some of which is systematic, as will be discussed.

In an "atom in a molecule" formulation of the shielding for a second-row element such as nitrogen the paramagnetic term σ_p, which largely determines the chemical shift δ (the two being defined with opposite sign), is given by[15,38]

$$-\sigma_p = (2\mu_0/3\pi)\mu_B^2(\Delta E)^{-1}\langle r^{-3}\rangle_p P_i \qquad (1)$$

when one low-lying excited state is dominant, or if an effective

excitation energy may be used. The magnetic field mixes into the ground state those (p–p) excited states that involve charge circulation (are magnetic dipole allowed), the more so the lower the excitation energy ΔE. The paramagnetic circulations are the more effective (deshielding) the closer they are to the resonant nucleus ($\langle r^{-3} \rangle_p$ large) and the larger is P_i, the angular imbalance of charge in the valence shell (an angular momentum term).

Several factors combine to increase the range, or sensitivity, of the nitrogen shifts in nitroso or nitrosyl compounds. P_i is large for a bent planar group (and decreases with decrease in the MNO angle). The n(N) $\rightarrow \pi^*$(NO) state is particularly low-lying since the HOMO is largely nonbonding, and the LUMO is low because of the electronegativity of nitrogen and oxygen. The p(N) electron radius (r_p) is reduced by the electronegative substituent oxygen but is increased by delocalization into d orbitals in the complex: the influence of the radial term $\langle r^{-3} \rangle$ is a quasi-nephelauxetic, or electron-cloud-expanding, effect.

For a transition metal the corresponding formulation is[15,38]

$$-\sigma_p = (2\mu_0/3\pi)\mu_B^2 (\Delta E)^{-1} \langle r^{-3} \rangle_d D_i \qquad (2)$$

where D_i is now the imbalance of charge in the d shell, ΔE represents an effective (or weighted mean) ligand field splitting,[39] and r is the d-electron radius. The deshielding of the metal nucleus is mediated by paramagnetic circulations of d electrons, and is greater the closer the d electrons to the metal nucleus and the smaller the energy or energies of d–d excitation. The D_i term takes a maximum value of 12 when three d orbitals are filled and two are empty (d^6) or vice versa (and varies rather little for a given coordination geometry and similar ligands), whereas P_i takes a maximum value of 2. The very large shift range observed for cobalt can thus be related to its position in the periodic table:[15] ligand field excitation energies tend to be lower in the first transition series than in the second or third, the radial factor $\langle r^{-3} \rangle_d$ increases across the series with increase in effective nuclear charge, and the angular imbalance is large in the open d shells.

The energy term gives the shifts a "spectrochemical" dependence, the shielding tending to decrease with decrease in the ligand field splitting. Indeed, the nitrogen and cobalt shielding was observed to decrease with decrease in energy of the visible absorption band (to which d–d and M $\rightarrow$ L charge-transfer excitations contribute) in the bent nitrosyls so far documented (dithiocarbamate, acacen, salen, etc.).[7] Following the spectrochemical series,[40] the shielding would be expected to decrease in the sequence of ligating atoms N > O > S. The radial factor, however, imposes a nephelauxetic influence, tending to decrease the shielding as S > N > O, with decrease in delocalization (from the softer to the harder ligand).[40] The two influences therefore combine to decrease the shielding N > O (i.e., for ligands from the same row) but are in opposition for ligands from different rows of the periodic table.[15] For partially filled d shells, as in these nitrosyls, the nephelauxetic influence dominates for ligands from different rows (and for ligands from the same row the two influences may be confused). As Table I shows, the cobalt shielding tends to decrease in the sequence of basal ligating atoms, $S_4 > S_2N_2 > N_4 > $ OONN > ONON.

Of particular interest is the degree to which these trends appear in the nitrogen as well as the cobalt shielding, given the selective influences also present. These include the medium effects on the projecting nitrosyl, which are less important at the cobalt nucleus as the coordination geometry is little affected; and the direct influence on the cobalt shielding, but not on the nitrogen shielding, of d–d circulations in the basal plane, as explained below.

The highest shielding is observed with sulfur coligands, and may be explained by their higher nephelauxetic effect. The lowest shielding is observed for the most electronegative coligating atoms. Table I shows that the shielding is decreased by further intro-

duction of electron-withdrawing substituents and that electron donor substituents have the opposite effect. The nitrogen and cobalt shielding are reduced (and the NO stretching frequency increased) in the salox complexes, with oxygen attached to the ligating nitrogen, compared to the salen complexes, and reduced also with electronegative substituents in the phenylene rings. Conversely, higher shielding is observed in each series when alkyl substituents are present, in a chelate ring (ketox vs. salox, 7-Mesalen vs. salen) or in a phenylene ring. (Similarly, the cobalt shielding in tris(dithiocarbamates) is higher the more electron donating the alkyl groups.[41]) Corresponding effects of (Me, OMe, Cl) substituents on the NO stretching frequency were observed early on in [Co(NO)(salen)] derivatives.[18] Deshielding appears to be associated also with electron withdrawal by phenyl, phenylene, or other aromatic rings in the ligand, as in the sequence (in ^{15}NO shielding) of the N_4 ligands (en)$_2$ > amben > TPP, and from acacen to benacen or salen, or from salen to salphen.

Overall, deshielding tends to correlate with reduction in strength of covalent bonding to the metal. Here, as in other series of compounds, low shielding of the metal nucleus correlates with instability of the complex.[42] Conversely, covalency (and nephelauxetism) are higher for the complexes with ligating sulfur.

The introduction of a nephelauxetic parameter β, derived from optical spectroscopy, into the shielding equation, has been achieved for a group of cobalt(III) complexes with ligating F, O, N, C, Cl, and Br.[43] The energy term was expressed as h/β, where h is the energy of the first (lowest energy) d–d band, and the radial function as $\langle r^{-3} \rangle_d / \beta$. β is defined as the ratio of the values of the Racah (interelectron repulsion) parameter B in the complex and in the gaseous metal ion, and is obtained from the interval between the first and second d–d bands. A good fit to the shielding equation, extrapolating to the value of the magnetogyric ratio for ^{59}Co, was obtained for orthoaxial complexes, in which the ligands lie on the Cartesian axes, but greater scatter arises with the distorted geometries of chelating ligands.[43] This is a further factor that contributes to the blurring of the trends observed for the nitrosyls under discussion. Thus the dithiocarbamate ligand has a smaller bite than the others in Table I, and the points for the dithiocarbamate complexes lie above the lines determined by the other compounds in Figures 2 and 3.

Mixing of Nitrosyl and Ligand Field Orbitals. Interdependence of the ^{15}N and ^{59}Co shielding is a consequence of the matching of π^*(NO) and d orbital energies, and extensive mixing of the orbitals, which explains the range of MNO geometries.[12,13] The low-lying π^*(NO) orbitals are excellent d-electron acceptors, and $d\sigma^*$(M–N) electron density in [MNO]^8 complexes can be stabilized as a lone pair on nitrogen in the bent ligand.

Energy level diagrams have been calculated by the Wolfsberg–Helmholtz method for [Co(NO)(NH$_3$)$_5$]$^{2+}$ and related ions with different coordination geometries,[12] and by the extended Hückel method for nitrosyl bonded to five-coordinate iridium,[13] to show the orbital interactions as the nitrosyl ligand bends. These results have been adapted in Figure 4 so as to show, schematically, the interrelation of the magnetically active excitation energies for ^{15}N and ^{59}Co in the bent nitrosyls. The d energy levels on the left of the diagram are appropriate to the umbrella shape of the basal ligand in the square pyramids: the cobalt is 0.1–0.5 Å above the plane of the coligating atoms, in the complexes in Table I. The z^2 orbital is stabilized by s,p mixing so as to point more in the direction of the vacant site trans to the nitrosyl and is assumed to lie below the π^*(NO) levels. The sequence and separation of the energy levels depend on the coligands and the details are not known, but the general conclusions are independent of these.

The two d orbitals in the MNO plane, the z^2 and xz, are the ones most strongly involved. Figure 5 shows their interaction with the n' orbital (with σ-NO symmetry) and π^*_{xz}(NO) orbital of

(38) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714.
(39) Ionov, S. P.; Lyubimov, V. S. *Russ. J. Phys. Chem. (Engl. Transl.)* **1971**, *45*, 1407.
(40) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, England, 1962. Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.

(41) Bond, A. M.; Colton, R.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1985**, *24*, 1298.
(42) Green, J. C.; Grieves, R. A.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1313.
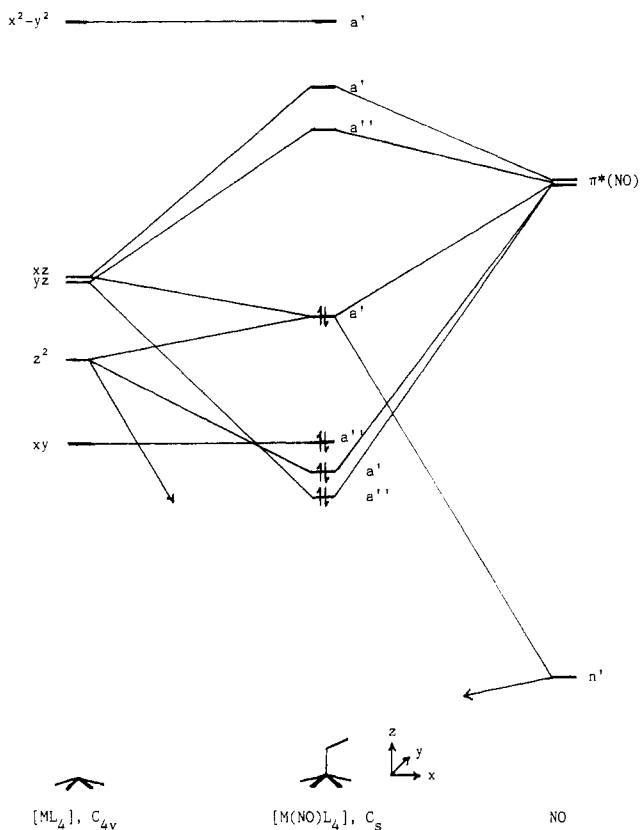(43) Bramley, R.; Brorson, M.; Sargeson, A. M.; Schäffer, C. *J. Am. Chem. Soc.* **1985**, *107*, 2780.

Figure 4. Scheme showing interactions of n'(N), π*(NO), and ligand field orbitals in a square-pyramidal complex with bent apical nitrosyl.

Figure 5. a–c Diagrams showing interactions of n'(N) and π*(NO) with d_{z^2} (a), d_{xz} (b), and d_{yz} (c) orbitals. (d) Diagram to illustrate a major paramagnetic circulation on nitrogen.

the ligand. As can be seen in Figure 5a, the destabilizing interaction of the filled z^2 and n' orbitals is alleviated by MNO bending to ca. 125° for the nitrosyls in question, and a bonding interaction of the z^2 and π^*_{xz}(NO) orbitals then develops. Bending to this angle reduces the back-bonding from xz to π^*_{xz}(NO) (Figure 5b), while the back-bonding in the yz plane is only slightly reduced (Figure 5c).

Thus the "lone pair" on nitrogen consists of nonbonding electron density in the MNO plane, which in the HOMO in Figure 4 is delocalized in π^*_{xz}(NO), xz, and z^2 orbitals. Figure 5d is a perspective view of the most important paramagnetic circulation determining the nitrogen shift, effectively n(N) → π*(NO), using the a″ LUMO (in Figure 4) formed from the π^*_{yz} and yz orbitals (Figure 5c). The atomic circulation at nitrogen shown in Figure 5d is of $p_{z'}$ → p_y type, with the $p_{z'}$ orbital at an angle of 35° to the z axis for a 125° MNO angle. In-plane and out-of-plane paramagnetic circulations of n'(σ-NO) → π*(NO) type contribute also. The HOMO in Figure 3 is destabilized by the interaction with the z^2 orbital, the more so with better (σ + π) donation from the basal ligands. Thus weaker coligands reduce the nitrogen as well as the cobalt shielding, and coordination of a sixth ligand may have a similar effect. (If the z^2 orbital is sufficiently high lying, then the mainly π*(NO) orbitals are occupied in preference to ligand field orbitals.) Clearly, multiple factors are at work, but the extensive mixing of the π*(NO) LUMOs with the z^2, xz, and yz orbitals acts to increase the nitrogen and the cobalt shielding as back-bonding increases.

Thus nephelauxetic and spectrochemical effects are interconnected for the two nuclei. Strictly, nephelauxetism is defined for d electrons,[40] but it clearly has an analogue for nonbonding p electrons such as the "lone-pair" electrons on nitrogen. The
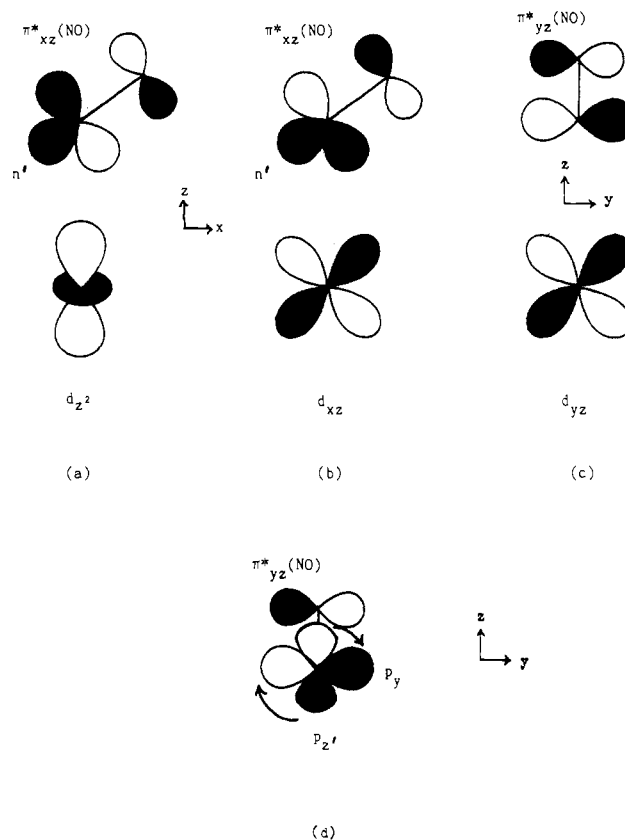
parallelism of eq 1 and 2 makes this point in the context of nuclear magnetic shielding. There is evidence for similar mutualities in other metal–ligand combinations,[15] but the matching of the orbital energies enhances such effects for these cobalt nitrosyls.

Selective, or independent, influences on the nitrogen and the cobalt shielding have been mentioned as contributing to the scatter in Figures 1–3: these are, notably, medium effects, and distortions from axial symmetry in the coordination sphere. Further, the angular imbalance of charge in the nitrogen valence shell (P_i) is clearly but not simply connected with that for cobalt (D_i). Particularly important is the $xy → x^2 - y^2$ circulation in the basal plane. This deshields cobalt but not nitrogen (cf. the increased shielding of protons attached to transition metals) and is highly sensitive to the nature of the basal ligands. Thus in Figure 3 the complexes with basal N_4 ligation would be better fitted by a line below the one drawn, displaced toward higher cobalt shielding, as expected from the higher nephelauxetism of N_4 compared to that of O_2N_2 ligators.

Overall, however, it is clear that the ligand field effects that mediate the ^{59}Co shielding are linked with the factors controlling the ^{15}N shielding, and the NMR results offer further support for the theoretical description of the bent nitrosyl complexes.