

>> Thd, Urd. This order of interaction is probably the result of a combination of several factors, including site nucleophilicity, "class b" acid-base interactions, and steric interactions.

The results presented here demonstrate that metal interactions with thiolated guanosine derivatives can significantly alter the acidities of protons bonded to ring nitrogen atoms. These perturbations could have drastic effects on the extent

to which thiolated nucleic acid derivatives are involved in hydrogen bonding when incorporated in nucleic acids and could readily lead to base mispairing. The phenomena discussed here could be important in defining the role of thiolated guanine derivatives as antitumor agents.

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Nitrogen-15 and Cobalt-59 NMR Study of the Bent Nitrosyl Ligand in Cobalt Complexes

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The strongly bent nitrosyl ligand, with an MNO angle around 120°, differs markedly from the linear ligand in spectroscopic properties. ¹⁵N shifts are reported for 5-coordinate cobalt(III) complexes with Schiff base (salen, acacen, benacen, ketox, salox) or dithiocarbamate basal ligands and bent apical nitrosyl ligands. As in C-nitroso groups, the nitrogen is strongly deshielded (by 500–800 ppm) relative to comparable linear nitrosyls. The ¹⁵NO and ⁵⁹Co shielding tends to decrease with a decrease in the MNO angle and in the energy of the longer wavelength electronic absorption. The relatively low cobalt shielding is consistent with other evidence that the strongly bent nitrosyl is a weaker ligand than linear nitrosyl. Nitrosyls with intermediate angles appear to have intermediate properties.

Introduction

The bent nitrosyl ligand in transition-metal complexes has been more elusive than might have been expected, on the analogy of the main-group XNO compounds, since NOX angles between 105 and 120° are found for C- or N-nitroso compounds, nitrites, thionitrites, nitrosyl halides, and so on. Most transition-metal nitrosyls¹ have nearly linear MNO groups, in which the ligand is formally NO⁺, isoelectronic with CO. Back-bonding then gives an M=N=O contribution reminiscent of the bonding in N₂O and NO₂⁺, which are linear; indeed, the linear nitrosyl ligand heads the "spectrochemical series" (based on IR spectroscopy) of π-acceptor ligands.² This property can be linked with the relatively low energy of the π*(NO) orbital, arising from the electronegativity of nitrogen and oxygen.

Much less is known about the bent nitrosyl ligand, and a purpose of the present work has been to use ¹⁵N and ⁵⁹Co NMR, in conjunction with electronic spectroscopy, to make comparisons with better known ligands. A strongly bent nitrosyl (with IrNO angle 124°) was characterized by X-ray crystallography in 1968;³ strong MNO bending in [Co(NO)(S₂CNMe₂)₂] was indicated earlier⁴ and has since been confirmed.⁵ A dozen or so such {MNO}⁸ complexes have now been characterized with square-pyramidal or octahedral coordination. They can be described in terms of a lone pair on the nitrogen and a d⁶ metal, so that the ligand is formally NO⁻. The (MNO)ⁿ description is useful for partially bent nitrosyls with a less obvious distribution of n_N and d electrons, as in mononitrosyls with an odd n_N electron and dinitrosyls with distorted NMN and MNO angles.¹

The ease of bending of MNO, in contrast to MCO or MN₂, can also be related to the low energy of the π*(NO) orbital, which is comparable with the energies of the d orbitals with which it overlaps.⁶ The bending, as an intramolecular redox

process, has mechanistic and catalytic significance, since the shift of a d-electron pair onto nitrogen can allow nucleophilic attack on the metal and electrophilic attack on the nitrosyl.⁷

Many problems have arisen in the characterization of bent nitrosyls. This is a very labile group so there are preparative difficulties, crystallographic (rotational) disorder is common, and thermal motions are particularly large for the oxygen. The structure may change from solid to solution (the energy barrier being small),⁸ and there is a sizeable overlap of NO stretching frequencies for bent and linear MNO.⁹

The gap can now be filled by ¹⁵N NMR spectroscopy. It has long been known that nitrogen carrying a lone pair of electrons in a delocalized system, as in main-group nitroso and nitrosyl compounds, is deshielded by low-energy n_N → π* circulations in the magnetic field.¹⁰ The deshielding of 300 ppm or more from NNO to R₂NNO, or from NO₂⁺ to RONO,¹⁰ suggested a nitrogen NMR criterion for MNO bending. A dramatic dependence of the nitrogen shift on the MNO angle was found, with deshieldings of up to 800 ppm for strongly bent compared with linear cobalt nitrosyls¹¹ and intermediate deshieldings for intermediate MNO angles in dinitrosyls.¹² Such deshielding can also be used as a criterion

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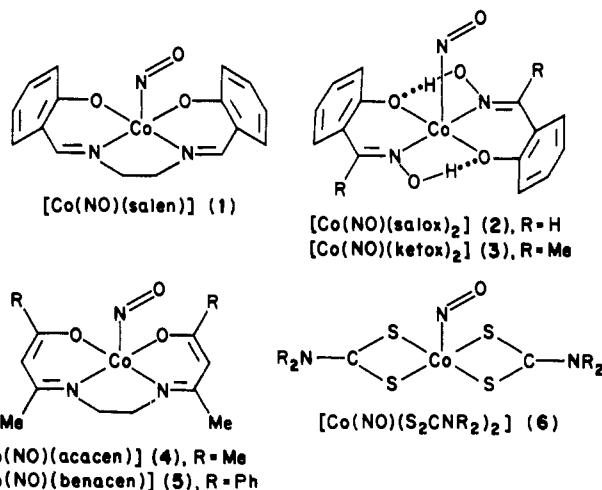
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of bending at the ligating nitrogen in transition-metal diazenido complexes.¹³

Several linear nitrosyls have been measured in ¹⁴N resonance, ¹⁴⁻¹⁶ since the symmetry reduces ¹⁴N quadrupolar broadening. ¹⁴N lines are broadened when the nitrogen carries a lone pair, and with increase in correlation time, as with bulkier coligands.¹⁰ The use of ¹⁵N ($I = 1/2$) gives sharp lines but raises problems of low natural abundance (0.365%) and slow relaxation in the absence of nearby protons. Linear nitrosyls in piano-stool complexes of Cr, Mo, and W were, however, measured in natural abundance of ¹⁵N, with a (180-MHz) wide-bore spectrometer, by Legzdins, Roberts, and co-workers.¹⁷

Our initial studies of the bent nitrosyl ligand in square-pyramidal complexes of cobalt with Schiff base (salen (1)),^{18,19}



salox (2), ketox (3),²⁰ acacen (4),²¹⁻²³ benacen (5)^{21,23} or dithiocarbamate (6)⁵ coligands were done in natural abundance of ¹⁵N, on a wide-bore 180-MHz spectrometer. The work proved very difficult because of slow relaxation, solubility limitations, and decomposition during long acquisition times, so we turned to a 400-MHz spectrometer and 99% ¹⁵N enrichment. This has the advantage of distinguishing products of decomposition of the nitrosyl group, which we are currently investigating. Cobalt complexes were chosen for this study so that ⁵⁹Co NMR spectroscopy could throw further light on the properties of the nitrosyl ligand, from comparisons with related complexes of the Schiff base or dithiocarbamate ligands.²⁴⁻²⁷

Experimental Section

¹⁵N spectra in natural abundance were measured on nearly saturated solutions in 25-mm tubes on a Bruker WH 180 spectrometer. [Cr(acac)₃] was added to promote relaxation, unless decomposition became evident; acquisition times were 17-65 h. Spectra with 99% ¹⁵N enrichment were run on a Bruker WH 400 spectrometer.

¹⁴NO was generated from sodium nitrite and acidified iron(II) sulfate. ¹⁵NO was supplied by Prochem Ltd. Solvents were rigorously dried and deoxygenated, and inert atmospheres were used.

The salenH₂, acacenH₂, and benacenH₂ ligands were prepared by literature methods.^{18,22,23} The oxime of 2-hydroxyacetophenone was prepared by the reaction of hydroxylamine hydrochloride with the ketone in 96% ethanol containing pyridine. Sodium diethyldithiocarbamate was obtained from BDH Chemicals Ltd. Sodium dimethyl- and diisopropylidithiocarbamates were obtained by the action of carbon disulfide in chloroform on an aqueous solution of sodium hydroxide and the appropriate amine.²⁸ Satisfactory analyses were obtained for the known salen,¹⁸ acacen,^{22,23} and benacen²³ nitrosyl complexes.

N,N'-Ethylenebis(salicylideneaminato)[(¹⁵N)nitrosyl]cobalt, [Co(¹⁵NO)salen] (1). The general method¹⁸ for this class of nitrosyl is to mix solutions of cobalt(II) acetate and the organic ligand under NO at 1 atm pressure, but much lower pressures can be used (to economize ¹⁵NO) since the reaction is irreversible. Cobalt(II) acetate tetrahydrate (0.21 g, 0.84 mmol) was dissolved in DMF (5 cm³) and the reaction flask evacuated. ¹⁵NO (23 cm³) was transferred in from a gas buret and salenH₂ (0.25 g, 0.93 mmol) added from a side arm. When the mixture was stirred and shaken, crystals of [Co(¹⁵NO)salen] separated after 1 h. The solution was warmed and residual ¹⁵NO in connecting tubing swept into the reaction flask with nitrogen. The crystals were filtered off under nitrogen and washed with ethanol, a further crop being obtained by addition of ethanol to the filtrate. The slight excess of salen and ¹⁵NO prevents contamination with [Co(salen)].

N,N'-Ethylenebis(benzoylacetone iminato)[(¹⁵N)nitrosyl]cobalt, [Co(¹⁵NO)benacen] (5), was prepared²³ from cobalt(II) acetate tetrahydrate (0.21 g, 0.84 mmol) dissolved in methanol (8 cm³) and benacenH₂ (0.32 g, 0.92 mmol) suspended in acetone (8 cm³). When the solutions were mixed under ¹⁵NO (ca. 23 cm³), a brown solid separated. The reaction was slow so the mixture was stirred, shaken frequently over several hours, and then left overnight. The black crystals obtained were filtered off, washed with 1:1 methanol/acetone and dried under vacuum.

Bis(2-hydroxyacetophenone oximato)[(¹⁵N)nitrosyl]cobalt, [Co(¹⁵NO)(ketox)₂] (3). Solid 2-hydroxyacetophenone oxime (0.26 g, 1.72 mmol) was added to a stirred suspension of cobalt(II) acetate tetrahydrate (0.21 g, 0.84 mmol) in 96% ethanol (20 cm³) under ¹⁵NO (ca. 25 cm³). The solution darkened, and black crystals of the nitrosyl soon separated. The mixture was heated gently until all the acetate in suspension had reacted and then left overnight. The black crystals were filtered off, washed with ethanol, and dried under vacuum. The unlabeled compound²⁰ was prepared similarly under an excess of ¹⁴NO. Anal. Calcd for C₁₆H₁₆N₃O₅Co: C, 49.4; H, 4.1; N, 10.8. Found: C, 49.5; H, 3.9; N, 10.7.

Bis(2-hydroxyacetaldoximato)[(¹⁵N)nitrosyl]cobalt, [Co(¹⁵NO)(salox)₂] (2), was prepared by a method analogous to the one used for [Co(NO)(ketox)₂]. The unlabeled compound had satisfactory microanalyses. Anal. Calcd for C₁₄H₁₂N₃O₅Co: C, 46.5; H, 3.3; N, 11.6. Found: C, 46.7; H, 3.2; N, 11.6.

N,N'-Ethylenebis(acetylacetone iminato)[(¹⁵N)nitrosyl]cobalt, [Co(¹⁵NO)(acacen)] (4), was prepared by the addition of aqueous cobalt(II) acetate to *N,N'*-ethylenebis(acetylacetone imine) in methylated spirits under ¹⁵NO.^{22,23}

Bis(*N,N'*-dialkyldithiocarbamate)[(¹⁵N)nitrosyl]cobalt Complexes, [Co(¹⁵NO)(S₂CNR₂)₂] (6) (R = Me, Et, *i*-Pr), were prepared as above by the slow addition with stirring of the sodium dialkyldithiocarbamate dissolved in methanol to cobalt(II) acetate tetrahydrate in the same solvent under ¹⁵NO.²⁹ Purer nitrosyls have been obtained by use of [Co(NO)(en)]₂(ClO₄)₂,^{5,30,31} but this would have been less convenient with ¹⁵NO.

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Table I. ¹⁵N NMR, IR, and Structural Measurements of Nitrosyl Complexes

| compd | solvent | δ(¹⁵ N) ^a | MNO/deg | NO/ Å | MN/ Å | ν- (¹⁴ NO) ^b / cm ⁻¹ | λ/nm | ε | ref | |
|---|---|--|-----------------|----------|--------------|--|-----------|------|----------|----------|
| | | | | | | | | | struct | UV/vis |
| Bent Nitrosyls | | | | | | | | | | |
| [Co(¹⁵ NO)(S ₂ CNEt ₂) ₂] | CDCl ₃ | 500.8 | ... | ... | ... | 1625 1615 ^d | 370 | 5000 | ... | 29 |
| [Co(¹⁵ NO)(S ₂ CNMe ₂) ₂] | CDCl ₃ | 501.3 | 135.1 | 1.17 | 1.75 | 1625 1595 ^d | black | | 5 | |
| [Co(¹⁵ NO)(S ₂ CN- <i>i</i> -Pr ₂) ₂] | Me ₂ SO CD ₂ Cl ₂ | 502.6 526.9 | 129 | 1.11 | 1.71 | 1637 1606 ^d | | | 30 | |
| [Co(¹⁵ NO)(acacen)] (4) | CDCl ₃ CDCl ₃ CDCl ₃ Me ₂ SO | 510.3 ^c 507.8 ^c 521.9 714.3 | 122.4 | 1.09 | 1.82 | 1654 1655 ^e | 480 | 680 | 21 | 23 |
| [Co(¹⁵ NO)(benacen)] (5) | Me ₂ SO CD ₂ Cl ₂ | 723.0 724.7 | 122.9 | 1.14 | 1.83 | 1635 1630 ^f 1605 ^d | 520 | 980 | 21 | 23 |
| [Co(¹⁵ NO)(salen)] (1) | CDCl ₃ CD ₂ Cl ₂ | 726.8 725.4 | 127.0 (mean) | 1.15 | 1.81 | 1624 1626 ^f 1595 ^d | 550 | 870 | 19 | 23 |
| [Co(¹⁵ NO)(ketox) ₂] (3) | Me ₂ SO CD ₂ Cl ₂ | 736.9 741.1 ^g | 126.3 | 1.11 | 1.81 | 1675 1645 ^d 1635 ^f | black | | 32 | |
| [Co(¹⁵ NO)(salox) ₂] (2) | CDCl ₃ CDCl ₃ Me ₂ SO | 740.3 ^h 717.9 ^{c,g} 824.1 ^g | ... | ... | ... | 1672 1645 ^d | black | | ... | |
| Linear Nitrosyls ⁱ | | | | | | | | | | |
| [Ru(NO)(NH ₃) ₅]Cl ₃ | H ₂ O | -29 ^j | 172.8 | 1.17 | 1.77 | 1913 | | | <i>k</i> | |
| Na ₂ [Fe(CN) ₅ (¹⁵ NO)] | H ₂ O | -13.5 | | | | 1944 | red-brown | | | |
| [Co(CO) ₃ (NO)] | C ₆ H ₆ | 14 ^{l,m} | 180 | 1.10 | 1.76 | 1805 | 374 (red) | 640 | <i>n</i> | <i>o</i> |
| <i>trans</i> -[RhCl(¹⁵ NO)(P- <i>i</i> -Pr ₃) ₂](ClO ₄) | CDCl ₃ | 24.0 ^p | ... | ... | ... | 1842 | | | <i>q</i> | |
| [Ru(¹⁵ NO) ₂ (PPh ₃) ₂] | C ₆ D ₆ | 50.7 ^r | 170.6 177.7 | 1.19 | 1.78 1.76 | 1615 1665 | red | | <i>s</i> | |
| [Rh(NO)(¹⁵ NO)(PPh ₃) ₂](ClO ₄) | CD ₂ Cl ₂ | 81.4 ^r | 158.9 | 1.16 | 1.82 | 1714 1759 | black | | <i>t</i> | |

^a Relative to neat liquid nitromethane, high-frequency positive; normally measured at 25 °C, with 99% ¹⁵N enrichment, 400-MHz spectrometer. ^b Nujol mull, unless a solvent is specified. ^c In natural abundance of ¹⁵N, 180-MHz spectrometer. ^d ν(¹⁵NO) in nujol mull. ^e In CHCl₃. ^f In Me₂SO. ^g Broadened by unresolved coupling to ⁵⁹Co. ^h Partially resolved octet, ¹J(⁵⁹Co¹⁵N) = 9 Hz. ⁱ If ¹⁵N is not indicated, ¹⁵N was measured by wide-line methods, and the uncertainty may be 10 ppm or so because of broad lines and referencing uncertainties. ^j Reference 15. ^k Bottomley, F. J. *Chem. Soc., Dalton Trans.* 1974, 1600. ^l Reference 14. ^m Reference 16. ⁿ Brockway, L. O.; Anderson, J. S. *Trans. Faraday Soc.* 1937, 33, 1233. ^o Clark, R. J. *Inorg. Chem.* 1967, 6, 299. ^p Reference 11. ^q Calderon, J. L.; Cotton, F. A.; Legzdins, J. *J. Am. Chem. Soc.* 1969, 91, 2528. ^r Reference 12. ^s Gaughan, A. P.; Corden, P. J.; Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* 1974, 13, 786. ^t Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* 1975, 14, 3070.

Results and Discussion

Bent and Linear Nitrosyl Ligands. Table I gives spectroscopic and MNO structural^{5,19-21,30,32} measurements for square-pyramidal cobalt complexes with bent apical nitrosyl and chelating basal coligands, with some values for linear nitrosyls for comparison. [Co(NO)(salox)₂] (2) and [Co(NO)(ketox)₂] (3) are new nitrosyls,²⁰ the first examples of the type [Co(NO)(oximate)₂] in which the basal ligands are bidentate phenolate anions of salicylaldehyde or a derivative of this, including 2-hydroxyacetophenone oxime. The conformation of the bent nitrosyl, though susceptible to the demands of crystal packing, is of interest, as a tendency has been noted for the nitrosyl to bend in the plane of best π acceptance of the coligands.³³ In the acacen and benacen complexes the apical nitrosyl lies above a Co-N bond in the plane²¹ and in the S₂CNMe₂ complex the oxygen lies above a sulfur atom,⁵ but in the ketox complex it lies above the centre of one of the chelate rings.³²

Although 5-coordinate complexes are often fluxional in solution, none of the spectra reported here show any signs of fluxionality (as, for example, we have observed⁸ in the IR and NMR spectra of solutions of [RuCl(NO)₂(PPh₃)₂], which has

one bent and one linear nitrosyl in the solid state). The quadridentate Schiff base ligands are not flexible when coordinated, and the ketox and salox nitrosyls also are kept as square pyramids by strong hydrogen bonds between the basal ligands.³²

The value of the nitrogen shift as a criterion of bending of the nitrosyl is clearly evident in Table I. Linear nitrosyls of Fe, Co, Ru, and Rh absorb at medium field near the free ligand NO⁺ (δ -5).³⁴ The strongly bent nitrosyls are further deshielded by 500-800 ppm, as are C-nitroso compounds;³⁵ δ(¹⁵N) is 594 for *t*-BuNO.¹² The slightly bent dinitrosyls, with MNO angles down to 160°, are slightly deshielded¹² relative to the linear mononitrosyls.

Table I also demonstrates an angle dependence of the nitrogen shielding among the strongly bent nitrosyls. Although the MNO angle, like the conformation, is sensitive to crystal forces and may be different in the solution and the solid,⁸ the smaller ¹⁵N deshielding for the dithiocarbamate compared with the Schiff base complexes seems to reflect a larger MNO angle and more back-bonding with coligating sulfur. Shorter M-NO bonds and larger MNO angles are commonly found

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with softer (As, S) compared with harder (N, O) coligands,¹ the bending increasing with σ - or π -donor ability of the basal ligands.⁶ Thus, electron-attracting ring substituents in [Co(NO)(salen)] were found to increase the NO stretching frequency, consistent with decrease in back-bonding from the metal to NO⁻.¹⁸

That the nitrogen deshielding on bending increases with a decrease in the ligand field splitting is shown by greater deshielding for complexes of cobalt than for complexes of Ru, Rh, Os, Ir, etc.,^{8,11} as ligand field splittings increase from the first to the second or third transition series. The higher ¹⁵N shielding in the dithiocarbamate relative to the Schiff base complexes should then correlate with higher ⁵⁹Co shielding (greater splitting of the ligand field), as we observe.

The ¹⁵N shifts of the bent nitrosyls extend the known range for diamagnetic nitrogen compounds by 200 ppm.³⁶ Organic diazene and nitroso compounds with nitrogen shifts in the range 500–600 ppm are deep blue or purple, the deshielding increasing as the $n_N \rightarrow \pi^*$ band goes to lower energies across the range of main-group NOX compounds.³⁵ Low-lying excited states involving rotation of charge close to nitrogen are present also in the nitrosyl complexes; the absorption bands given in Table I are not present in the parent Schiff base or dithiocarbamate complexes. On the preliminary evidence the nitrogen shielding in the cobalt nitrosyls appears to decrease as the visible band goes to lower energies, but more measurements are needed to establish the correlation. Interestingly, [Co(NO)(benacen)] gives a two-step reduction wave with $E_{1/2}^{\text{red}}$ values of -1.04 and -1.43 V, compared with -1.46 V for [Co(benacen)], suggesting that the LUMO at nitrogen is lower than at the metal.²³

Electronic spectra of 6-coordinate Co(III) complexes with a strongly bent nitrosyl ligand, [CoX(NO)(LL)₂]⁹ (LL = en, das; X = halide, MeOH, etc.)³⁷ were interpreted as showing ligand-to-metal charge transfer and ligand field bands comparable to those of corresponding complexes with halide replacing NO⁻,^{38,39} indicating that NO⁻ lies between Br⁻ and I⁻ in the spectrochemical series.³⁷ A lone pair on the ligating atom is expected to reduce the ligand field splitting and also to increase the nephelauxetic effect⁴⁰ for NO⁻, which would otherwise be relatively small because of the high electronegativity. But, NO⁻ differs from a halide ligand in being a weak to moderate π acceptor and quite a strong σ donor, with a strong trans weakening effect, on the evidence of M–N and N–O bond shortening, and the long bond (or absence) of a trans ligand.⁴⁵ A better comparison for NO⁻ is with the azide ligand, which is bent at the ligating nitrogen (but has little or no π -acceptor properties) and has been placed between F⁻ and Cl⁻ in the spectrochemical series.⁴⁰

Cobalt-59 Shielding in the Nitrosyl and Related Complexes. Table II gives the ⁵⁹Co shifts and line widths for the bent nitrosyls and for some related (Schiff base, dithiocarbamate, cobaloxime)^{24–27} complexes, with some linear nitrosyls⁴¹ and dinitrosyls⁴² for comparison. The quadrupolar line widths are difficult to rationalize, since they depend on the product of the square of the electric field gradient at the ⁵⁹Co nucleus

Table II. ⁵⁹Co NMR Measurements of Cobalt Nitrosyl and Related Complexes

| complex | solvent | $\delta(^{59}\text{Co})^a$ | $W_{1/2}^b/$ Hz | ref |
|---|--|----------------------------|--------------------|-----|
| Linear Nitrosyls (etc.) | | | | |
| H[Co(CO) ₄] | pentane | -3720 | | 41 |
| [Co(NO)(CO) ₃] | heptane | -1365 | | 41 |
| [Co(NO) ₂ Br] ₂ | CH ₂ Cl ₂ | 3390 | | 42 |
| [Co(NO) ₂ Cl] ₂ | CH ₂ Cl ₂ | 3640 | | 42 |
| Bent Nitrosyls (etc.) | | | | |
| [Co(S ₂ CNEt ₂) ₃] | | 6450 | 300 | 27 |
| [Co(¹⁵ N)(S ₂ CNEt ₂) ₂] | CDCl ₃ | 6642 | 1150 | |
| [Co(¹⁵ N)(S ₂ CNMe ₂) ₂] | CDCl ₃ | 6668 | 750 | |
| | Me ₂ SO | 6906 | 2150 | |
| [Co(S ₂ CNMe ₂) ₃] | | 6775 | | 26 |
| [Co(Me)(H ₂ O)(dmgH) ₂] | MeOH | 4020 | | 25 |
| [Co(Me)(H ₂ O)(acacen)] | MeOH | 7150 | | 25 |
| [Co(Me)(acacen)] | CH ₂ Cl ₂ | 7420 | | 24 |
| [Co(¹⁵ N)(acacen)] | CDCl ₃ | 8001 | 1700 ^c | |
| [Co(¹⁵ N)(benacen)] | CD ₂ Cl ₂ | 8170 | 2550 | |
| | CDCl ₃ | 7449 | 5800 ^c | |
| [Co(Me)(H ₂ O)(salen)] | MeOH | 6820 | | 25 |
| [Co(Me)(salen)] | CH ₂ Cl ₂ | 7175 | | 24 |
| [Co(¹⁵ N)(salen)] | CDCl ₃ | 7658 | 11700 ^c | |
| | Me ₂ SO | 8100 | | |
| [Co(¹⁵ N)(ketox) ₂] | CDCl ₃ | 8478 | 240 ^d | |
| | CDCl ₃ + HClO ₄ | 8528 | 3030 ^c | |
| | Me ₂ SO | 9390 | 4000 | |
| [Co(¹⁵ N)(salox) ₂] | CDCl ₃ | 8586 | 3000 | |
| | Me ₂ SO | 8966 | 2700 | |

^a Relative to K₃[Co(CN)₆](aq), high-frequency positive. ^b Approximate line width at half-height. ^c Proton broad-band decoupled. ^d Well-resolved septet. ⁴J(⁵⁹Co¹H) = 540 Hz.

($I = 7/2$) and the correlation time (inverse tumbling rate). Occasionally quite sharp ⁵⁹Co lines were observed, as for [Co(¹⁵N)(ketox)₂]. This gave a well-resolved septet for the ⁵⁹Co resonance due to coupling with the methyl groups. Partially resolved coupling to ⁵⁹Co was also observed in the ¹⁵N resonance, and the ¹⁵N line in the salox compound was broadened by unresolved coupling (Table I). Very small electric field gradients at the central nucleus can sometimes arise in ligand environments that appear irregular.⁴³

Correlations of increased shielding of a transition-metal nucleus with increase in ligand field strength and nephelauxetic ability of the ligands are now well documented.^{27,44} Table II shows that cobalt is deshielded in the bent nitrosyl complexes by upwards of 8000 ppm relative to the complexes with stronger ligands such as linear NO and CO (even though lower shielding is generally observed for tetrahedral than octahedral coordination, for comparable ligands). The dinitrosyls are intermediate, as might be expected. Thus, the trend of the cobalt shielding resembles that of the ¹⁵N shielding, reflecting the interdependence⁶ of the frontier orbital gap (for charge rotation) at the two nuclei.

Rather similar cobalt shielding is observed for 5-coordinate Co(III) in the dithiocarbamate nitrosyls with coordination sphere [CoNS₄] and for 6-coordinate cobalt [CoS₆] in the corresponding tris(dithiocarbamate) compounds.^{26,27} Similarly, the cobalt shielding in the Schiff base nitrosyls [CoN₃O₂] resembles that observed for [CoN₆], [CoN₅O], and [CoN₄O₂] octahedral Co(III) complexes (cf. also [Co(NO₂)₆]³⁻ with $\delta(^{59}\text{Co})$ 7440).²⁷ The addition of a sixth ligand such as H₂O or an amine to [Co(Me)(acacen)] or [Co(Me)(salen)] (cf. Table II) also affects the shielding rather little, given that the total range of ⁵⁹Co shifts is 19 000 ppm. [CoO₆] compounds such as [Co(acac)₃]³⁻ and [Co(CO₃)₃]³⁻ have cobalt shifts in the range 12 500–14 000.²⁷

Clearly, the cobalt shifts in the bent nitrosyls are strongly dependent on the nature of the basal ligands. The increase in cobalt shielding from Schiff base (acacen or salen) to co-

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baloxime complexes reflects an increase in ligand field splitting, in parallel with increased stability with respect to dissociation.²⁵ Interestingly, the salox and ketox nitrosyls were the least stable during the long acquisition times of our natural-abundance measurements.

The ⁵⁹Co data for the acacen, salen, and cobaloxime complexes with a range of axial ligands,^{24,25} together with the similarities in ⁵⁹Co shielding for NO⁻ and dithiocarbamate ligands, support the description of NO⁻ as a fairly weak ligand, particularly if its nephelauxetic effect is larger than that of other nitrogen ligands such as amines (azide has been placed between Br⁻ and I⁻ and below dithiocarbamate in a nephelauxetic series⁴⁰).

Table II shows a slight but consistent trend to lower ⁵⁹Co shielding if Me₂SO is used instead of chloroform for the 5-coordinate nitrosyls, and this may indicate weak coordination

by Me₂SO. There are indications also of ¹⁵N deshielding and lower NO stretching frequency with a more basic solvent; trans coordination would be expected to increase the tendency for MNO to bend.

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Synthesis, Characterization, and X-ray Molecular Structures of Mono- and Dinuclear Copper Complexes with 2,7-Bis(2-pyridyl)-1,8-naphthyridine

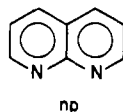
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The preparation and characterization of two complexes of 2,7-bis(2-pyridyl)-1,8-naphthyridine (bnpn) with copper(II) and copper(I) are described. The X-ray molecular structure of a mononuclear Cu(I) complex, [Cu(bnpn)(PPh₃)₂]PF₆, was determined with full-matrix least-squares procedures to a final *R* index of 0.057. Crystals are monoclinic, space group *P*2₁/*n*, with cell dimensions *a* = 14.855 (6) Å, *b* = 21.914 (8) Å, *c* = 15.111 (2) Å, and *V* = 4862.651 Å³ with *Z* = 4. The X-ray molecular structure of the dinuclear complex [Cu₂(bnpn)(μ-Cl)(μ-OH)Cl₂] was also determined to a final *R* index of 0.0363. The crystals are monoclinic, space group *P*2₁/*m*, with cell dimensions *a* = 7.694 (1) Å, *b* = 16.434 (2) Å, *c* = 7.921 (1) Å, and *V* = 952.695 Å³ with *Z* = 2. In the latter complex, each Cu(II) ion is chelated by a 2,2'-bipyridine fragment of the bnpn and the two metal ions are linked by bridging chlorine and oxygen atoms. The Cu-Cu distance is 3.022 Å. The coordination geometry about each Cu(II) is approximately a square pyramid with the bridging chlorine as the apical ligand and two nitrogen atoms, one bridging oxygen atom, and a terminally bound chlorine atom as the four basal ligands of the square pyramid. Magnetic susceptibility measurements of the paramagnetic complex suggest a weak antiferromagnetic interaction ($|2J| < 200 \text{ cm}^{-1}$, room-temperature magnetic moment/Cu = 1.64 μ_B), which couples the spins of the two unpaired electrons. Cyclic voltammograms of this complex in aqueous solution show reduction occurs in two one-electron transfers (*E*_{1/2} = 0.36, 0.16 V vs. Ag/AgCl). X-ray photoelectron spectroscopy allows differentiation of bridging vs. terminal chlorine atoms with peaks at 197.2 (5) and 196.2 (2) eV, respectively. Preliminary studies show that in situ reduction of the bnpn copper(II) dimer gives solutions of bnpn copper(I) dimers that reversibly coordinate carbon monoxide.

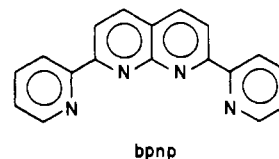
Introduction

Binucleating ligands that can coordinate two metal centers in close proximity have been the subject of considerable experimental interest.² One promising dinucleating system utilizes 1,8-naphthyridine (np) as the bridging unit. However,



while several dinuclear np complexes have been characterized,³

the more common coordination of this bidentate ligand is the chelation of a single metal ion.⁴ Recently, Caluwe reported the preparation of 2,7-bis(2-pyridyl)-1,8-naphthyridine (bnpn).⁵ Dinuclear complexes of this relatively rigid tetra-



dentate ligand would be crescent shaped and in principle have

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