Synthesis and ^{15}N Nuclear Magnetic Resonance Shift Tensors of Bent Nitrosyl Complexes with *N*-Substituted Salicylideneiminate Coligands; the Shift Tensor as a Criterion of MNO Bond Angle†

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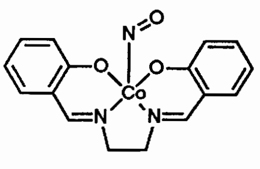
A series of nitrosylcobalt–Schiff base complexes [Co(NO)(asal)$_2$] [asal = *N*-alkyl- or *N*-aryl-salicylideneiminate, *o*-OC$_6$H$_4$CH=NR, R = Me(msal), Et(esal), Bu^n(bsal), Ph(phsal) or CH$_2$Ph(bzsal)] has been prepared. Single-crystal X-ray structure analysis of the esal derivative shows the molecule to be pyramidal with a bent apical nitrosyl group [Co–N 1.738(12), N–O 1.16(2) Å, Co–N–O 129(1)°] and a *trans* arrangement of the basal ligands [Co–O 1.833(6), Co–N 1.950(6) Å]. The crystals are orthorhombic, space group *Pbca*, *a* = 9.544(3), *b* = 17.000(3), *c* = 11.359(3) Å, *Z* = 4; the structure was refined to *R* = 0.059 for 822 observed reflections. The compounds are not very stable in solution, but high-resolution cross-polarisation magic-angle spinning ^{15}N NMR spectroscopy of the [Co(^{15}NO)(asal)$_2$] solids, and also of [Co(^{15}NO)(ketox)$_2$](ketox = *o*-OC$_6$H$_4$CMe=NOH), shows large isotropic shifts (*ca.* 730 ppm relative to nitromethane) characteristic of bent nitrosyls. Also characteristic are the nitrogen shift tensors, with one very large component (1100–1960 ppm) reflecting the low energy of the n(N) $\longrightarrow$ π*(NO) circulation. The large ranges of the shielding anisotropy Δ (540–1150 ppm) and the asymmetry parameter η (1.25–2.40) reflect the sensitivity (because of the low excitation energies) of the tensor components to relatively small changes in the geometry of the MNO group, and its relation to the ligands in the basal plane.

The outcome of nitrosation reactions in co-ordination chemistry is not readily predictable, because of the lability of co-ordinated NO in redox processes, and because of the versatility of the nitrosyl ligand, which may be linear, 120°-bent, semi-bent (as in the presence of other non-innocent ligands), bent-linear fluxional in solution, dihapto, or bridging as M$_2$(NO) or M$_3$(NO).[1]

In five-co-ordinate $\{MNO\}^8$ complexes [*i.e.* with 8 (d + n) electrons] the metal may have a trigonal-bipyramidal co-ordination sphere (d^8) with the nitrosyl linear (NO$^+$), or a square-pyramidal co-ordination sphere (d^6) with bent apical nitrosyl (NO$^-$). In the cobalt nitrosyl Schiff-base complexes which we reported earlier[2,3] a square-pyramidal structure was maintained by the lack of flexibility of a four-co-ordinate ligand in the basal plane, as in [Co(NO)(salen)] **1** [salen = *N,N'*-ethylenebis(salicylideneiminate)] or by strong hydrogen bonding of two chelate ligands, as in [Co(NO)(ketox)$_2$] **2** (ketox = *o*-OC$_6$H$_4$CMe=NOH). Sometimes, however, the isomeric forms are similar in stability, as for [CoCl$_2$(NO)(PR$_3$)$_2$][4,5] and [RuCl(NO)$_2$(PPh$_3$)$_2$]$^+$,[5] and in the latter complex rapid bent-linear fluxionality of the two nitrosyls in solution was demonstrated by ^{15}N NMR studies in solution and in the solid state.[6,7]



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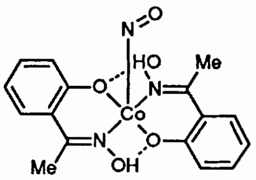

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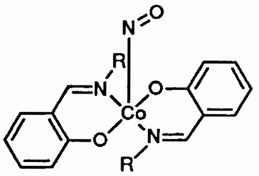

3	R	asal
	Me	msal
	Et	esal
	Bu^n	bsal
	Ph	phsal
	CH$_2$Ph	bzsal

We now report studies of [Co(NO)(asal)$_2$] complexes **3** containing *N*-alkyl or *N*-aryl-salicylideneiminate Schiff-base ligands *o*-OC$_6$H$_4$CH=NR which are not constrained to coplanarity, these being made from salicylaldehyde and an amine (*n*-alkylamine, aniline or benzylamine). The parent complexes [Co(asal)$_2$] mostly have tetrahedral co-ordination,[8] except that the *N*-methyl ligand gives dimeric complexes [{Co(asal)$_2$}$_2$] (with oxygen bridges) in which the metal is co-ordinated by three oxygens and two nitrogens (O$_3$N$_2$) in a distorted trigonal-bipyramidal arrangement.[9] These complexes slowly oxidise in air, so reaction with NO was tried. This gave the nitrosyls **3**, and we report an X-ray crystallographic structure for the esal derivative.

We have found that nuclear magnetic deshielding of the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and physical data for the new nitrosyl complexes [Co(NO)(asal)$_2$]

		Analysis (%)*			
asal	M.p./°C	C	H	N	δ(^{1}H)(CDCl$_3$)
msal	decomp.	53.3 (53.8)	4.6 (4.5)	11.1 (11.8)	3.75 (6 H, CH$_3$), 6.5 (2 H, s, CH), 6.9–7.8 (8 H, aromatic H)
esal	85–86	56.9 (56.1)	5.3 (5.2)	11.8 (10.9)	0.5–1.8 (6 H, s, C*H*$_3$CH$_2$), 3–4.2 (4 H, s, CH$_3$C*H*$_2$), 5.8–8 (10 H, CH and aromatic H)
bsal	56–57	59.7 (59.9)	6.65 (6.4)	9.8 (9.5)	0.5–1.9 (14 H, CH$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 3.2–3.9 (4 H, s, C*H*$_2$CH$_2$CH$_2$CH$_3$), 6.3–7.8 (10 H, CH and aromatic H)
phsal	50.5	64.7 (64.9)	4.25 (4.2)	8.5 (8.7)	
bzsal	180–181	66.4 (66.0)	4.8 (4.75)	8.6 (8.25)	1.25 (4 H, s, CH$_2$Ph), 6.2–7.3 (10 H, CH and aromatic H)

* Calculated values in parentheses.

Table 2 Final atomic parameters for non-hydrogen atoms in [Co(NO)(esal)$_2$], with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Co	0.500	0.500	0.500
O(1)	0.6374(7)	0.5752(4)	0.4929(5)
O(2)	0.481(1)	0.5756(6)	0.299(1)
N(1)	0.3974(6)	0.5590(3)	0.6194(5)
N(2)	0.428(1)	0.5526(7)	0.384(1)
C(1)	0.5614(8)	0.6674(4)	0.6318(6)
C(2)	0.6537(8)	0.6406(4)	0.5479(7)
C(3)	0.7726(9)	0.6877(5)	0.5218(7)
C(4)	0.7946(8)	0.7564(5)	0.5770(8)
C(5)	0.7031(9)	0.7825(4)	0.6603(9)
C(6)	0.5857(8)	0.7386(4)	0.6892(8)
C(7)	0.4420(9)	0.6247(4)	0.6639(6)
C(8)	0.260(1)	0.5287(5)	0.6665(7)
C(9)	0.1426(9)	0.5521(7)	0.587(1)

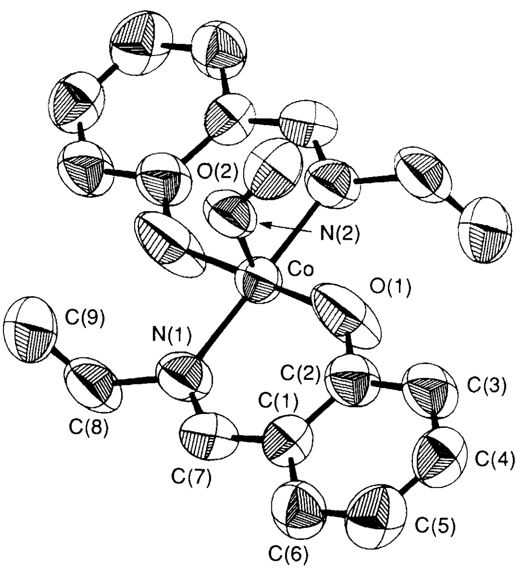

Fig. 1 Molecular structure of [Co(NO)(esal)$_2$]

Table 3 Selected bond lengths (Å) and angles (°) for [Co(NO)(esal)$_2$], with e.s.d.s in parentheses

Co–O(1)	1.833(6)	O(1)–Co–N(1)	91.8(3)
Co–N(1)	1.950(6)	O(1)–Co–N(2)	83.8(4)
Co–N(2)	1.738(12)	N(1)–Co–N(2)	93.7(4)
O(1)–C(2)	1.285(10)	Co–O(1)–C(2)	132.0(6)
O(2)–N(2)	1.16(2)	Co–N(1)–C(7)	123.3(5)
N(1)–C(7)	1.297(9)	Co–N(2)–O(2)	129(1)
N(1)–C(8)	1.504(11)	C(2)–C(1)–C(7)	122.0(6)
C(1)–C(2)	1.376(11)	O(1)–C(2)–C(1)	123.1(7)
C(1)–C(7)	1.400(11)	N(1)–C(7)–C(1)	127.8(7)
C(8)–C(9)	1.494(13)		

nitrogen[10] is a good criterion of MNO bond angle in nitrosyls[2,3,6,7,11,12] as in diazenido[13] and related groups, since the development of lone-pair electron density on the nitrogen gives rise to low-energy paramagnetic circulations of n(N) ⟶ π type, the more so the greater the degree of bending. The NO stretching frequency is not a useful criterion because of overlap of the ranges for linear and bent ligands. Compounds **3**, however, were found to be unstable in solution, so were examined by solid-state ^{15}N NMR spectroscopy (with 99% ^{15}N enrichment of the nitrosyl). This has afforded the first opportunity for detailed study of the shift tensors of a range of nitrosyl complexes, the previously reported[2] compound **2**, with a Co–N–O angle of 126°,[14] being included for comparison.

Results and Discussion

All the evidence points to a square-pyramidal geometry with bent apical nitrosyl **3** for the new complexes, as shown in Fig. 1 for [Co(NO)(esal)$_2$], studied by single-crystal X-ray crystallography. The analytical and ^{1}H NMR data are given in Table 1. Repeated efforts were made to obtain suitable crystals for X-ray crystallography of all the compounds studied, but were successful only for the esal compound.

Molecular Structure of [Co(NO)(esal)$_2$].—Final atomic parameters for this complex are given in Table 2 and selected bond lengths and angles in Table 3. As shown in Fig. 1 the basal ligands have a *trans* arrangement (ONON co-ordination). The Co–N–O angle is 129(1)°, *i.e.* the group is 'strongly' bent, as shown also by the ^{15}N shielding tensors; the oxygen lies over a gap between the two esal ligands. The Co–N–O angle and Co–N and N=O bond lengths are within the ranges found previously for square-pyramidal nitrosyls with ONON, OONN or N$_4$ co-ordination in the plane.[2,3] The nitrosyl is disordered in the crystal, and occupies sites equally either side of the basal plane. Since the cobalt lies on a centre of symmetry, as demanded by the space group, it must lie in the basal plane when the atomic positions are averaged over all unit cells. This is in contrast to other nitrosyls of this type, in which the cobalt is found 0.2–0.3 Å out of the basal plane, displaced towards the nitrosyl group;[2,3] in **2** the cobalt is 0.3 Å above the plane.[14] In such cases the U_{ii} coefficients of the thermal parameter are substantially unequal, with the long axis of the vibrational ellipsoid perpendicular to the basal plane. In [Co(NO)(esal)$_2$] however the U_{ii} coefficients are almost equal, resulting in a near-spherical vibration ellipsoid (Fig. 1).

IR Spectroscopic Measurements.—The new nitrosyl complexes all have ^{14}NO stretching frequencies (Table 4) in the region expected for strongly bent Co–N=O groups. In each case the stretching frequency is lowered by 25–40 cm^{-1} on substitution of ^{15}N, but overlap of the ν(^{15}NO) band with

Table 4 Spectroscopic and magnetic properties of square-pyramidal nitrosyl complexes of cobalt

	^{15}N NMR parameters[a]								$\nu(^{14}NO)$	^{59}Co NMR parameters[b]		
Complex	δ_{soln}[c]	δ_{solid}	Method[d]	δ_{11}	δ_{22}	δ_{33}	Δ[e]	η[f]	cm^{-1}	δ_{soln}[c]	$W_{\frac{1}{2}}$/Hz	μ_{eff} (T/K)
$[Co(^{15}NO)(msal)_2]$	n.o.	734.6	HBSR	1 139(42)	690(35)	374(46)	541(70)	1.25(0.16)	1 650	n.o.	—	0.7 (298) 0.6 (87)
			MWM	1 178	625	401	500	1.66				
$[Co(^{15}NO)(esal)_2]$	739.7	741.9	HBSR	1 959(13)	240(21)	26(16)	1 073(25)	2.40(0.03)	1 645	9 662 11 001[g]	1 150 313	0.5 (290)
			MWM	1 906	402	−83	1 237	1.82				
$[Co(^{15}No)(bsal)_2]$	740.5	728.2	HBSR	1 262(39)	669(39)	254(43)	712(65)	1.25(0.13)	1 665	9 675 11 042[g]	2 000 345	1.0 (289)
			MWM	1 277	702	206	783	1.10				
$[Co(^{15}NO)(phsal)_2]$	n.o.[h]	719.9	HBSR	1 212(21)	604(22)	344(26)	564(40)	1.61(0.08)	1 645	9 238	2 200	0.7 (298) 0.5 (85)
			MWM	1 220	607	333	580	1.58				
$[Co(^{15}NO)(bzsal)_2]$	530.2	721.9	HBSR	1 922(11)	291(12)	−47(16)	1 154(24)	2.12(0.02)	1 665	9 380	2 000	0.7 (289)
			MWM	1 915	221	30	1 038	2.45				
$[Co(^{15}NO)(ketox)_2]$[i]	740.3[j,k]	781.3	HBSR	1 124(9)	871(5)	348(12)	649(18)	0.58(0.02)	1 675	8 478[j,l]	240	

[a] δ values are in ppm relative to neat liquid nitromethane; n.o. = not observed. [b] δ values are in ppm relative to $[Co(CN)_6]^{3-}$(aq). [c] In CD_2Cl_2. [d] Method of spinning side-band analysis for the extraction of tensor components (see text). The HBSR uncertainties express 95% confidence intervals, the MWM uncertainties are *ca.* ± 100 ppm. [e] $\Delta = \frac{1}{2}(\delta_{11} + \delta_{22}) - \delta_{33}$. [f] $\eta = (\delta_{11} - \delta_{22})/(\delta_{iso} - \delta_{33})$. [g] Probably due to the $[Co(o\text{-}OC_6H_4CH{=}NR)_3]$ compound (see Discussion). [h] Possibly very weak signals at δ 550 and 536. [i] Measured by C. Brévard. [j] In $CDCl_3$. [k] Octet, $J(^{59}Co\text{–}^{15}N)$ = 9 Hz. [l] Seven lines resolved.

Table 5 Cobalt-59 NMR data for $[Co(asal)_3]$ complexes in CD_2Cl_2

asal	$\delta(^{59}Co)$	$W_{\frac{1}{2}}$/Hz
msal	10 627	416
bsal	11 038	403
phsal	11 235	1 090
bzsal	10 925	570

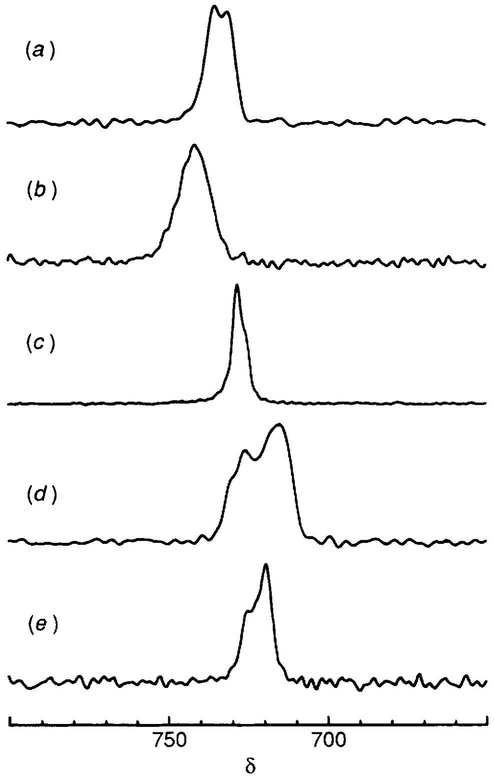

Fig. 2 The ^{15}N CP MAS solid-state NMR centre-band resonances of $[Co(NO)(asal)_2]$ compounds, asal = msal (*a*), esal (*b*), bsal (*c*), phsal (*d*) or bzsal (*e*)

ligand absorption then prevents accurate measurement of the frequency.

Magnetic and NMR Measurements.—The magnetic moments of the complexes (Table 4) resemble those observed for [Co(NO)(salen)] **1** and its derivatives.[15] The decrease as the temperature is lowered shows that the moments can be ascribed to Van Vleck ('temperature-independent') paramagnetism. The relatively large magnitudes, for spin-paired compounds, is indicative of low-lying magnetically active excited states, and so accords with the low nuclear magnetic shielding[16] of nitrogen and cobalt, shown in Table 4.

The ^{59}Co shifts of the nitrosyls are all rather similar, the linewidths reflecting the size of the molecule as well as the relatively low symmetry of the co-ordination sphere. The cobalt signals observed for $[Co(^{15}NO)(o\text{-}OC_6H_4CMe{=}NOH)]$, however, were unexpectedly narrow, with resolution of the H,D isotopomers (seven lines), and unusually, an octet due to $^{59}Co-^{15}N$ coupling was resolved in the ^{15}N spectrum; it seems that the cobalt has relatively high electronic symmetry in this compound (*cf.* the low asymmetry parameter, η = 0.58).

Evidence of decomposition was observed in the solution NMR spectra of the $[Co(^{15}NO)(asal)_2]$ compounds. The msal complex gave no ^{15}N or ^{59}Co resonance in solution, and the phsal complex gave no ^{15}N resonance. The ^{59}Co NMR spectra of the esal and bsal complexes contained an additional weaker and sharper resonance near δ 11 000, representing a cobalt compound containing no ^{15}N (Table 4). The strong deshielding, as observed for cobalt(III) complexes with O_6, N_6 or mixed O,N co-ordination, suggests that the decomposition product may be $[Co(asal)_3]$ {*cf. fac*-$[Co(NH_3)_3(H_2O)_3]^{3+}(aq)$ has $\delta(^{59}Co)$ 10 600 ppm and $W_{\frac{1}{2}}$ 350 Hz}, for which the relatively symmetrical co-ordination sphere would be expected to give a relatively narrow line. This assignment was confirmed by preparation of $[Co(asal)_3]$ compounds (by published methods[8]), for which the ^{59}Co shifts, near 11 000 ppm, and the linewidths, are given in Table 5

The large isotropic ^{15}N shifts (δ_{soln} and δ_{solid}) of the $[Co(^{15}NO)(asal)_2]$ complexes, 720–740 ppm, resemble those of other square-pyramidal cobalt nitrosyls, *cf.* 740–830 ppm for ONON [ketox or salox ($o\text{-}OC_6H_4CH{=}NOH$)] coligands, 710–820 ppm for OONN (acen* or salen) coligands, and 700–770 ppm for N_4 ($H_2NCH_2CH_2NH_2$, amben, or tpp*) coligands; these represent deshieldings of up to 800 ppm for strongly bent compared with linear cobalt nitrosyls.[3]

^{15}N NMR Shift Tensors.—The $[Co(^{15}NO)(asal)_2]$ nitrosyls (except for the esal complex) show some splitting of individual side- and centre-bands, which appears to reflect some inequivalence of molecular sites. The splitting is shown for the centre bands in Fig. 2, being largest for the phsal compound, with overlapping peaks at δ 720.3 and 730.8. The compound $[Co(^{15}NO)(esal)_2]$ does not show a splitting because the disordered nitrosyl positions are symmetry-related, leaving the chemical environment of the ^{15}N unchanged. The ^{15}N splitting seen for the other compounds may be due to torsional disorder of the nitrosyl, in positions that are not symmetry-related. Owing to the high degree of overlap the total intensities were used in the side-band analysis, averaging the individual contributions, which are likely to be due to slightly differing NO conformations. As detailed in the Experimental section, both of the standard methods of spinning side-band analysis were used for extraction of the tensor components: the Herzfeld–Berger side-band ratio method (HBSR),[17] adapted for least-squares iteration by Hawkes *et al.*,[18] and the Maricq–Waugh moments method (MWM),[19] the latter with larger uncertainties (perhaps ±100 ppm). Fig. 3 shows the good agreement between the recorded and the simulated spectra. The tensor components and the values † of the anisotropy Δ and the asymmetry parameter η are given in Table 4.

The variations in the $[Co(^{15}NO)(asal)_2]$ tensor elements are unusually large, for closely related compounds. The nitrogen tensor, however, is expected to be very sensitive to the (rather variable) geometry and conformation of the MNO group, because of the small excitation energy,[21] or HOMO – LUMO gap (the HOMOs and LUMOs being the highest occupied- and lowest unoccupied-molecular orbitals) of the most important circulation deshielding the nitrogen, $n(N) \longrightarrow \pi^*(NO)$. Here n(N) represents the nitrogen lone-pair electron density, which has a major component perpendicular to the NO bond in the MNO plane, and components also in the CoN and NO bond directions.[3,10] A first approximation to the electron energy levels is given by the *ab initio* calculations reported for MeNO[22] (which have been shown pictorially[23]), as modified to take account of the extensive mixing of the nitrogen HOMOs and LUMOs with the cobalt d_{xz}, d_{yz} and d_{z^2} orbitals (where *z* is the pyramidal axis), which we discussed earlier in terms of the mixing of the ^{15}N and ^{59}Co paramagnetic circulations.[3]

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* acen Refers to Schiff-base ligands derived from acetylacetone and *N,N'*-ethylenediamine or substituted derivatives thereof. Examples include[2,3] acacen [*N,N'*-ethylenebis(acetylacetonateiminate)] and benacen [*N,N'*-ethylenebis(benzoylacetonateiminate)]; amben = *N,N'*-ethylenebis(2-aminobenzylideneiminate) and H_2tpp = 5,10,15,-20-tetraphenylporphyrin.

† Different definitions have been proposed for Δ and η; those we have used (*cf.* Table 4) are given in ref. 10, p. 7, and in ref. 20.

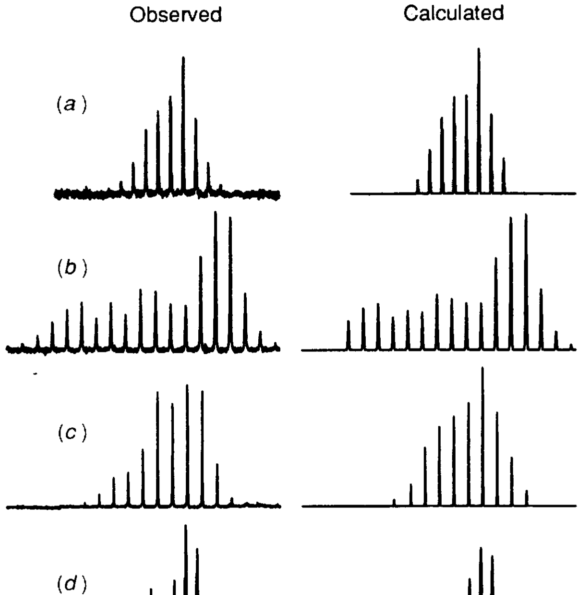

Fig. 3 The ^{15}N CP MAS solid-state NMR spectra of [Co(NO)(asal)$_2$] compounds, experimental and calculated spinning side-band patterns, asal = msal (*a*), esal (*b*), bsal (*c*), phsal (*d*) or bzsal (*e*)

In the linear nitrosyl ligand the MNO axis is one of high shielding, as for the MCO axis in a terminal carbonyl ligand,[24] the circulation about this axis in the magnetic field having relatively little paramagnetic component. The perpendicular elements reflect deshielding by $\sigma \longleftrightarrow \pi$ circulations of MN, n(N) and NO electrons, with values of 145–173 ppm for complexes of ruthenium with phosphine coligands.[7] In a strongly bent nitrosyl, because of the importance of the (low-energy) n(N) $\longrightarrow$ π*(NO) circulation, the principal axes of the shift tensor may not coincide with either of the bond directions, but the axis of maximum deshielding (δ_{11}) probably lies close to the NO bond axis (x) so as to make best use of the low-lying π*(NO) LUMO. The largest component of the paramagnetic circulation is then the $y \longleftrightarrow z$ circulation (the z axis being taken in the MNO plane), and this also has n,σ(CoN) $\longrightarrow$ π*(NO) and π(NO) $\longrightarrow$ σ*(CoN) contributions. As shown in Table 4, the δ_{11} values are large and cover a large range, 1140–1960 ppm.

The $x \longleftrightarrow y$ circulation is less well placed for n(N) electron density, but includes circulations of n,σ(CoN) and n,σ(NO) electrons in the low-lying π*(NO) orbital, as well as π(NO) $\longrightarrow$ σ*(CoN, NO) circulations. The in-plane ($x \longleftrightarrow z$) circulations can make use of high-lying n(N) density and CoN and NO σ electrons, but the (σ*) LUMOs are now higher. For compounds **3**, δ_{22} and δ_{33} (in comparison with δ_{11}) vary over smaller overlapping ranges, 240–700 ppm and -50 to 370 ppm respectively, which do not overlap with the δ_{11} values.

In delocalised systems the out-of-plane axis is normally the axis of highest shielding (δ_{33}), reflecting the high energy of $\sigma \longrightarrow \sigma$* circulations. This may well be the case in the bent MNO group, despite the (lower-energy) contribution of n(N) $\longrightarrow$ σ* circulations, because of the availability of the low-lying π*(NO) orbital for both the in-plane axes (x and z). Tentatively, therefore, we can associate δ_{22} and δ_{33} with the z and y axes, respectively, although the values of these tensor components are not greatly differentiated, and this assignment might be reversed for some bent nitrosyl ligands. The δ_{33} values in Table 4 resemble those observed for the perpendicular components of linear nitrosyls.[7,24]

The [Co(NO)(asal)$_2$] compounds in Table 4 appear to fall into two groups. The esal and bzsal compounds show large shielding anisotropies ($\Delta \approx 1100$ ppm) and asymmetries ($\eta \approx 2.25$), compared with smaller values of Δ (540–710 ppm) and η (1.25–1.6) for the msal, bsal and phsal derivatives, and also for [Co(^{15}NO)(ketox)$_2$] (with even smaller η, 0.58). The larger anisotropies and asymmetries arise from an increase in δ_{11} and decrease in δ_{22}, δ_{33}. Overall, in the broad range of nitrosyl complexes, δ_{11} is expected to increase with decrease in MNO angle,[2,3] but the two complexes of known structure in this study go against this trend: the nitrogen tensor for [Co(NO)(esal)$_2$], with a larger MNO angle, 129°, has a large δ_{11} (1959), compared with 1124 ppm (and relatively small anisotropy and asymmetry factor) for [Co(^{15}NO)(ketox)$_2$], with a smaller MNO angle (126°).[14] For [Co(^{15}NO)(ketox)$_2$] the intermediate element δ_{22} is rather large, reducing Δ and η and increasing the isotropic shift.

There is no obvious correlation of tensor elements (or Δ or η) with the magnetic moment of the complex (which is highly sensitive to traces of paramagnetic impurity), with the NO stretching frequency, or with properties of the R substituent, such as bulk. There is, however, some correlation of the δ_{11} (but not δ_{22} or δ_{33}) values with the cobalt shift, δ_{11} and δ(^{59}Co) increasing in parallel in each of the two groups of compounds. Some correlation of the nitrogen and cobalt shifts in solution was remarked in our earlier work on bent nitrosyls (with an extended range of coligands), and attributed to the degree of overlap of the two paramagnetic circulations (mainly n $\longrightarrow$ π* at nitrogen, and d–d at cobalt), and the similar energies of the frontier orbitals.[3]

A structural explanation for the grouping of the [Co(^{15}NO)(asal)$_2$] and [Co(^{15}NO)(ketox)$_2$] tensors is not readily discernible at present, and preliminary results for comparable bent nitrosyls include intermediate values of Δ and η.[25] Appropriate tensor components are sensitive (because of large effects of relatively small changes in a small excitation energy[10,26]) to the internal MNO geometry, to departure from axiality of the MN bond (as in the structure shown in Fig. 1), to the location of cobalt relative to the basal plane, and to the conformation of the nitrosyl relative to the basal ligands. All these are rather variable in these compounds, under the influence of crystal-packing requirements. In bent (square-pyramidal) nitrosyls the NO group commonly lies over a poor π donor in the plane. In [Co(^{15}NO)(esal)$_2$] (Fig. 1) it lies above the gap between the nitrogen and oxygen of the two Schiff-base ligands, and similarly for the two oximato ligands in [Co(^{15}NO)(ketox)$_2$], but swinging of the nitrosyl is a low-energy process.[25]

We have the interesting situation with the bent nitrosyl ligand that the asymmetry parameter η approaches the value 3 with the approach to (accidental) axial symmetry, as the two smaller components (δ_{22} and δ_{33}) become more equal (the anisotropy Δ *decreases* from the bzsal to the esal compound, and from the bsal to the phsal compound, with increase in η). The axial symmetry in the linear ligand, however, corresponds to $\eta = 0$.

Experimental

Preparations.—The cobalt(II) Schiff-base complexes were prepared under nitrogen by reaction of bis(salicylaldehydato)-cobalt(II) dihydrate with the appropriate amine (the aldehyde and amines being commercial products). These known complexes[8] had satisfactory microanalyses, and were stored under nitrogen. The nitrosyls were made by the admission of NO to a flask under vacuum containing a solution of the cobalt(II) complex in methanol. The flask was connected to a gas burette which showed that the uptake of NO was approximately 1 mol per mol of complex. Analytical and physical data for these compounds are given in Table 1.

[Co(NO)(esal)$_2$]. The compound [Co(NO)(esal)$_2$] (1.15 g, 3.2 mmol) was dissolved in methanol (25 cm^3) under nitrogen, which was then pumped out and NO admitted. The solution darkened as NO was rapidly absorbed. To ensure completion of the reaction the solution was stirred for 2 h. Black *crystals* separated on standing. These were filtered off rapidly in air, washed with pentane and dried in a desiccator (yield 1 g, 80%). Crystals so prepared were found to be suitable for X-ray crystallography. Black crystals of [Co(NO)(bsal)$_2$] were similarly obtained in 30% yield from [Co(bsal)$_2$]. The complex [Co(NO)(bzsal)$_2$] was isolated as a dark green *powder* in almost 100% yield.

The complex [Co(NO)(phsal)$_2$] was isolated as a dark green *powder* in similar yield. It was also prepared from a mixture of cobalt(II) acetate tetrahydrate (1.31 g, 5.28 mmol) in dimethylformamide (20 cm^3) with *N*-phenylsalicylaldimine (2.11 g, 10.7 mmol) in the same solvent (10 cm^3) under an atmosphere of nitric oxide. The *N*-phenylsalicylaldimine ligand was obtained as a yellow solid by condensation of equimolar quantities of aniline and salicylaldehyde in hot 96% ethanol and recrystallisation from the same solvent.

The complex [Co(NO)(msal)$_2$] was obtained as a black powder by the same two methods, the first giving a 70% yield. Methanol was used as solvent in the second method. *N*-Methylsalicylaldimine (1.81 g, 13.4 mmol) in methanol (10 cm^3) was mixed with cobalt(II) acetate tetrahydrate (1.67 g, 6.72 mmol) in the same solvent (15 cm^3) under nitric oxide. *N*-Methylsalicylaldimine was prepared by the addition of salicylaldehyde (61.1 g, 500 mmol) to 20% aqueous methylamine (62.1 cm^3, 500 mmol). The mixture was refluxed for 30 min, cooled, extracted with diethyl ether, and the extract dried with anhydrous sodium sulfate. After filtration the ether was removed to leave a yellow oil, b.p. 229 °C.

To prepare the ^{15}N-labelled nitrosyls, the cobalt(II) complex (0.3–0.4 g) and methanol (5 cm^3) were placed in a flask attached to a gas burette containing ^{15}NO, generated from Na^{15}NO$_2$ (99 atom% ^{15}N). The flask was evacuated while the contents were frozen, and a slight excess of ^{15}NO was admitted. The flask was allowed to warm up and the contents stirred for about 1 h, after which nitrogen was admitted, and the labelled nitrosyl filtered off.

Infrared Spectra and Magnetic Measurements.—Infrared spectra were recorded for Nujol mulls of the complexes on a Perkin-Elmer 577 spectrometer. Magnetic measurements were made by the Gouy method as before.[15]

X-Ray Crystal Structure Determination of [Co(NO)(esal)$_2$].—A crystal of approximate dimensions 0.4 × 0.3 × 0.1 mm was mounted on a glass fibre, and cell parameters determined on an Enraf-Nonius CAD4 automatic diffractometer from 25 accurately centred reflections in the range $13 \leqslant \theta \leqslant 15°$. The intensity data were measured for one octant of reciprocal space in the range $1 \leqslant \theta \leqslant 25°$, index range $0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 13$, using the ω–2θ scan mode, scan speed 3.3° min^{-1}, scan width (0.75 + 0.35 tanθ) to a maximum count of 90 s. The total number of reflections measured was 1619 of which 822 had an intensity $I \geqslant 3\sigma(I)$. Following the usual Lorentz-polarisation correction, an empirical absorption correction was applied, using ψ data giving minimum, maximum and average corrections of 0.965, 0.999 and 0.983. Absences were observed for $0kl$ (k odd), $h0l$ (l odd) and $hk0$ (h odd), uniquely identifying the space group as *Pbca* (61).

Crystal data. C$_{18}$H$_{20}$CoN$_3$O$_3$, M = 385.3, orthorhombic, space group *Pbca* (61), a = 9.544(3), b = 17.000(3), c = 11.359(3) Å, U = 1843(3) Å^3, Z = 4, D_c = 1.389 g cm^{-3}, $F(000)$ = 800, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 9.47 cm^{-1}.

Structure solution and refinement. The intensities of the *hkl* reflections were systematically strong for the parity groups *ggg* and *uuu*, indicating that the Co atom was sited at a centre of symmetry, in keeping with four molecules per cell. This posed two problems: (*i*) a structure-factor calculation based upon Co alone would not produce calculated phases for the other parity groups, which would lead to multiple images in the F_o map, and (*ii*) the NO group must be 50% on either side of the molecule which itself is not centrosymmetric. Accordingly the MULTAN program[26] was run, and yielded 11 atoms including a ring structure. One structure factor/Fourier cycle served to produce the remaining atoms, and after inclusion of H atoms in calculated fixed positions (d_H = 1.0 Å, with fixed thermal parameters of B = 5.0 Å^2) isotropic convergence occurred at R = 0.131. The NO group was given an occupancy factor of 0.5. An absorption correction by the program DIFABS[27] reduced R to 0.121 (minimum, maximum correction 0.644, 1.419; average 0.959). 822 Reflections, for which $I \geqslant 3\sigma(I)$, were used in the full-matrix anisotropic refinement, initially with Co only, then with all non-hydrogen atoms. This converged at R = 0.059, R' = 0.083, S = 1.083, with a weighting scheme $w^{-1} = [\sigma(F)]^2 + (0.05F)^2 + 5.0$ in which the coefficients were adjusted to give a near-linear slope 0.99 for a plot of δR *versus* normal probability. No extinction correction was applied as the correction factor was very small. The H-atom positions were calculated after each refinement cycle, and the highest peak in the final difference Fourier map was 0.47 e Å^{-3}. Table 2 gives the final atomic parameters and Table 3 selected bond lengths and angles for the atom numbering scheme in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

NMR Spectroscopy.—The ^{15}N NMR spectra were measured with 99% ^{15}N enrichment of the nitrosyl. Solution ^{15}N and ^{59}Co NMR spectra were recorded on a Bruker 400 MHz spectrometer. Solid-state ^{15}N NMR spectra were recorded with the use of cross polarisation, dipolar decoupling, and magic-angle spinning (CP MAS) on a Bruker MSL-300 spectrometer. The ^{1}H and ^{15}N frequencies were 300.13 and 30.45 MHz respectively. Samples were spun in 7 mm alumina or zirconia rotors in a Bruker double-bearing probe at speeds of 3.0 to 4.3 kHz. Recycle times were 2 or 5 s and the contact time 10 ms.

The low magnetogyric ratio of ^{15}N relative to ^{1}H dictates a Hartmann–Hahn ^{15}N/^{1}H pulse-amplitude matching condition with large ^{15}N power level which can lead to probe arcing. The CP match was therefore set at low power (20–40 kHz nutation frequency) and the ^{1}H power stepped up for decoupling during acquisition (60 kHz). The Hartmann–Hahn match was located with a sample of ^{15}NH$_4$^{15}NO$_3$ (90% ^{15}N).

The ^{15}N chemical shifts were referenced to external liquid nitromethane (*via* ^{15}NH$_4$^{15}NO$_3$), high frequency positive, and were reproducible to ±0.2 ppm. The isotropic chemical shift (the intensity-weighted middle of the centre-band lineshape) was determined by the acquisition of spectra at different spinning speeds.

Spinning side-band analysis. The spinning side-band patterns were analysed to give the principal components of the chemical shift tensor by the Herzfeld–Berger side-band ratio method[17] as adapted for least-squares iteration by Hawkes *et al.*,[18] and extended also to cover large anisotropies. Error estimates were made by using the variance matrix data from the least-squares computer program[18] to give 95% confidence intervals. With the good signal-to-noise ratio in the spectra the error limits were found to be ±(10–45) ppm. The values obtained by the moments method[19] show good agreement, and are given for comparison in Table 4; for these, error estimation is more difficult and qualitative (say ±100 ppm).

Acknowledgements

Solid-state ^{15}N NMR spectra were obtained on the University of London Intercollegiate Service instrument at Royal Holloway and Bedford New College; we thank Dr. Christian Brévard of Bruker Spectrospin, Wissembourg, for early CP MAS measurements of [$Co(^{15}NO)(ketox)_2$]. We thank also Mlle Sylvie Meyer for the preparation of complexes **3**, Dr. Oliver Howarth for solution ^{15}N and ^{59}Co NMR spectra run on the SERC high-field service at the University of Warwick, Drs. Herzfeld and Berger for further information on their spinning side-band analysis program to cope with large anisotropies, Dr. Keith Sales (Queen Mary and Westfield College, London) for use of their HBSR program, and J. M. thanks the Leverhulme Trust for a fellowship, 1989–1991.

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Received 26*th March* 1992; *Paper* 2/01614A