# Synthesis of High-spin Five-co-ordinate Lewis-base Adducts of Bis(triazen-1-olato)cobalt(II). Studies of Reversible Dioxygen Binding†

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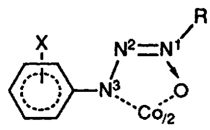
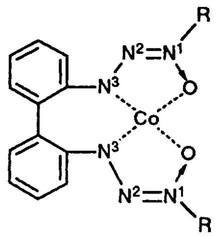
High-spin five-co-ordinate Lewis-base adducts of cobalt(II) triazene 1-oxide complexes have been prepared and their reactivity in reversible dioxygen binding studied. Monoclinic spin-Hamiltonian parameters are reported for the dioxygen complexes. An X-ray structure analysis of high-spin bis[3-(4-chlorophenyl)-1-methyltriazen-1-olato]cobalt(II)–pyridine (1/1) has been performed. The adduct crystallizes in the monoclinic system, space group *P*2/*c*, with *a* = 18.39(2), *b* = 12.553(9), *c* = 9.827(8) Å, β = 105.65(7)° and *Z* = 4. The co-ordination about the cobalt atom is distorted trigonal bipyramidal.

We have previously reported the formation of low- and high-spin four-co-ordinate bis(chelate)cobalt(II) triazene 1-oxide systems together with the results of X-ray investigations of low-spin bis(1-ethyl-3-phenyltriazen-1-olato)cobalt(II) which was shown to be square planar.[1] The possibility of reversible dioxygen binding in the presence of pyridine has also been preliminarily reported.

In this paper we describe the formation of high-spin, five-co-ordinate Lewis-base adducts of the above class of chelates and their reactivity towards dioxygen investigated by means of ESR spectroscopy. Some adducts were isolated and characterized as solids. The molecular structure of bis[3-(4-chlorophenyl)-1-methyltriazen-1-olato]cobalt(II)–pyridine (1/1) is also reported.

The investigations concerned two classes of four-co-ordinate complexes, *i.e.* bis(chelates) of bidentate triazene 1-oxides derived from aromatic monoamines and four-co-ordinate complexes of tetradentate triazene 1-oxides derived from 2,2′-diaminobiphenyl.





R = Me, Et, $Pr^n$, $Bu^t$ or Ph
X = H, 2- or 4-Me, 4-Cl, 4-Br, 4-$CO_2$Et, 4-$NO_2$, 4-OMe, or 2, 6-$Me_2$

R = Me, $Pr^n$ or $Bu^t$

## Experimental

Magnetic measurements were carried out by the Gouy (77–300 K) and Faraday (4.2–300 K) methods; $HgCo(SCN)_4$ was used as a calibrant and diamagnetic corrections were applied using Pascal's constants.[2]

Electronic spectra were recorded on a Beckman UV 5240 spectrometer, X-band ESR spectra on JES-3 (JEOL) and SE/X (RAdiopan) spectrometers equipped with an NMR magnetometer. The fourth $Mn^{2+}$ (MnO in MgO) was used as a *g* value calibrant. Frozen-solution spectra were measured in stoppered quartz tubes of 4 mm diameter at 77 K. Toluene solutions of Lewis bases were added using a microsyringe.

The oxygenation/deoxygenation cycles were carried out at *ca.* 210 K directly in the quartz tube used for ESR measurements using a thin Teflon tube connected with a syringe needle attached to the argon or dioxygen supply.

The SYMBAL program by Chmielewski *et al.*[3] was used for simulations of the ESR spectra of superoxo complexes. It allows for the monocyclic symmetry of the spin Hamiltonian.[4] The orientation dependence of the linewidth $\sigma_i$ has been assumed to be the same as for *A*. The linewidth has been found to be dependent on the spectral index $M_I$ as well. Thus σ has been represented by a polynomial with respect to $M_I$, including a quadratic term, with the polynomial coefficients assumed to be isotropic.

*Materials and Preparations of Ligands and Complexes.*—All chemicals were of reagent grade. Organic solvents were purified and dried using literature methods.[5] Solvents for spectral measurements were degassed by the double-syringe technique. Solid imidazoles were recrystallized from water, *N*-ethylimidazole was distilled under reduced pressure, and 4-cyanopyridine was recrystallized from 85% EtOH. Bidentate $XC_6H_4N_3ROH$ ligands were synthesized by the method of Bamberger and Renauld,[6] *i.e.* by coupling the appropriate aromatic diazonium salts with *N*-alkylhydroxylamines at 273 K at pH 3–4, followed by recrystallization from light petroleum (b.p. 40–60 °C), light petroleum–benzene or methanol (charcoal). Tetradentate 2,2′-$[C_6H_4N_3R(OH)]_2$ ligands were obtained according to the method of Behera and Chakravorty.[7]

The $[Co(ORN_3Ph)_2]$ and $[Co\{(ORN_3C_6H_4)_2\}]$ complexes were synthesized by reaction of the ligands and stoichiometric amounts of $Co(O_2CMe)_2{\cdot}4H_2O$ in boiling MeOH. All syntheses of cobalt(II) chelates and their adducts were carried out in an atmosphere of purified dinitrogen or argon. The details of the syntheses of the ligands and four-co-ordinate chelates are given elsewhere[8] and will be published separately. In this paper the synthesis of $4\text{-}ClC_6H_4N_3MeOH$ and its cobalt(II) complex are given in detail. Those of the remaining compounds are similar, only differing in the solvents used for ligand crystallization and the volumes of methanol used for chelate syntheses.

$4\text{-}ClC_6H_4N_3MeOH$. A solution (*ca.* 250 $cm^3$) of *N*-methylhydroxylamine acetate (0.2 mol) and sodium acetate (0.4 mol) in water (100 $cm^3$) was cooled to −10 °C. 4-Chloroaniline (25.5 g) was diazotized with $NaNO_2$ and added dropwise to the solution of *N*-methylhydroxylamine with vigorous stirring. The resulting yellow, darkening precipitate was filtered off, washed twice with

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† *Supplementary data available* (No. SUP 56877, 4 pp.): magnetic susceptibility data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

**Table 1** Analytical data and magnetic properties of [Co(ORN$_3$C$_6$H$_4$X)$_2$] Lewis-base adducts *

| | Analysis (%) | | | | μ | |
|---|---|---|---|---|---|---|
| Complex | C | H | N | X | 77 | 300 K |
| [Co(OMeN$_3$C$_6$H$_4$NO$_2$-4)$_2$]•2C$_5$H$_5$N | 47.5 (47.5) | 3.9 (3.95) | 23.5 (23.1) | | 4.29 | 4.42 |
| [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_5$H$_5$N | 45.2 (45.0) | 3.5 (3.7) | 19.7 (19.3) | 14.1 (14.0) | 4.10 | 4.30 |
| [Co(OMeN$_3$C$_6$H$_4$Br-4)$_2$]•C$_5$H$_5$N | 38.5 (38.3) | 3.2 (3.2) | 16.3 (16.4) | 26.8 (26.7) | 4.10 | 4.40 |
| [Co(OEtN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_3$H$_4$N$_2$ | 43.4 (43.6) | 4.0 (4.0) | 21.4 (21.4) | 13.8 (13.5) | 4.00 | 4.10 |
| [Co(OEtN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_5$H$_8$N$_2$ | 45.6 (45.7) | 4.7 (4.7) | 20.5 (20.9) | 13.1 (12.9) | 4.41 | 4.54 |
| [Co(OMeN$_3$C$_6$H$_4$Me-4)$_2$]•C$_3$H$_4$N$_2$ | 50.2 (50.1) | 5.0 (5.3) | 24.6 (24.6) | | 4.02 | 4.21 |
| [Co(OMeN$_3$C$_6$H$_4$Br-4)$_2$]•C$_3$H$_4$N$_2$ | 34.9 (35.0) | 3.0 (3.1) | 19.4 (19.7) | 27.0 (27.3) | 4.19 | 4.26 |
| [Co(OPhN$_3$C$_6$H$_4$Br-4)$_2$]•C$_5$H$_5$N | 48.2 (48.5) | 3.2 (3.2) | 13.5 (13.6) | 21.7 (22.2) | 4.08 | 4.23 |
| [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$] | 39.4 (39.3) | 3.5 (3.3) | 19.7 (19.6) | 16.5 (16.6) | 4.77 | 4.49 |

* Calculated values are given in parentheses; C$_5$H$_5$N = pyridine, C$_3$H$_4$N$_2$ = imidazole, C$_5$H$_8$N$_2$ = 1,2-dimethylimidazole.

water and dried in air. The crude product (14.5 g) was recrystallized from benzene–light petroleum (charcoal). Yield: 10 g.

[Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]. The ligand (1.15 g, 5 mmol) was dissolved in boiling methanol (16 cm$^3$) in an atmosphere of argon. The compound Co(O$_2$CMe)$_2$•4H$_2$O (0.622 g, 2.5 mmol) was dissolved in degassed methanol (10 cm$^3$) and added dropwise to the boiling solution of the ligand. Immediately a bright red precipitate deposited. The solution was cooled to 20 °C, the precipitate filtered off and washed twice with cool, degassed methanol (3 cm$^3$). Yield 1.3 g (90%). The elemental analyses and magnetic data are given in Table 1.

Pyridine mono- and di-adducts were prepared by recrystallization of the chelates from hot pyridine. They are unstable as solids and easily loose pyridine on standing. Only three mono- and one di-adduct giving satisfactory analytical results were isolated. The imidazole adducts were prepared by reaction of Co(O$_2$CMe)$_2$•4H$_2$O and the appropriate triazene 1-oxide in the presence of an excess of Lewis base. Also in this case it was difficult to obtain analytically pure adducts if a liquid base, *e.g.* *N*-ethylimidazole, was applied, a situation reported previously by Kennedy *et al.*[9] for substituted imidazole adducts of cobalt(II) Schiff-base complexes. Two typical procedures for adduct synthesis are presented below.

[Co(OEtN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_3$H$_4$N$_2$. The ligand (1.0 g, 5 mmol) and imidazole (0.680 g, 10 mmol) were dissolved in boiling MeOH (28 cm$^3$). After 10 min, Co(O$_2$CMe)$_2$•4H$_2$O (0.622 g) in MeOH (8 cm$^3$) was added dropwise. The solution became dark red. After cooling the resulting brown needles were filtered off, washed with cold EtOH (30 cm$^3$) and dried. Yield: 50%.

[Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_5$H$_5$N. The complex [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$] (0.600 g) was dissolved in boiling pyridine (10 cm$^3$). After 48 h dark red crystals separated at 258 K. Yield: 60%.

*X-Ray Crystal Structure Determination of* [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]•C$_5$H$_5$N.—*Crystal data.* C$_{19}$H$_{19}$Cl$_2$CoN$_7$O$_2$, $M$ = 507.2, monoclinic, space group $P2/c$, $a$ = 18.39(2), $b$ = 12.553(9), $c$ = 9.827(8) Å, β = 105.65(7)°, $U$ = 2184(4) Å$^3$, $D_m$ (by flotation) = 1.52 g cm$^{-3}$, $Z$ = 4, $D_c$ = 1.542(3) g cm$^{-3}$, $F$(000) = 1036, Mo-Kα radiation, λ = 0.710 69 Å, μ = 10.9 cm$^{-1}$.

A parallelepiped crystal of dimensions *ca.* 0.35 × 0.55 × 0.8 mm selected for data collection was placed in a capillary. Intensity data were recorded on a Syntex P2$_1$ automated diffractometer using graphite-monochromated Mo-Kα radiation. Intensities were measured using a 2θ–ω scan technique up to 2θ = 52°. The intensities of two standard reflections, monitored after every 50 intensity scans, showed no evidence of crystal decay. 4313 Reflections were collected, of which 2877 [$I \geqslant 3\sigma(I)$] were used for the structure determination. The data were corrected for background attenuation, Lorentz and polarization effects only.

*Structure determination and refinement.* The structure was solved by direct methods and refined by full-matrix least squares using the SHELX 76 program.[10] The hydrogen atoms were found from Fourier difference synthesis. The non-hydrogen atoms were kept anisotropic and hydrogens isotropic with the constraint that $d$(C–H) = 1.08 Å. The function minimized was $S = \Sigma w(F_o - F_c)^2$, where $w = 1/\sigma(F_o)^2$. Least-squares refinement converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.043 and $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$ = 0.050. Neutral-atom scattering factors were taken from ref. 11. The scattering factors for Co, Cl, O, N and C were corrected for real and imaginary components. The residual electron density was between −0.51 and 0.50 e Å$^{-3}$ and the maximum shift/e.s.d. ratio during the last cycle of refinement was 0.11 : 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

## Results and Discussion

*Adduct Formation.*—The four-co-ordinate complexes studied are, in the main, easily soluble in common non-co-ordinating solvents such as CH$_2$Cl$_2$, CHCl$_3$, benzene or toluene. The solutions reveal the presence of a narrow band at about 11 800 cm$^{-1}$ characteristic of low-spin square-planar cobalt(II) triazene 1-oxide complexes.[12] Addition of pyridine results in the disappearance of this band. This fact together with the absence of ESR signals in frozen pyridine and dimethyl sulfoxide solutions at 77 K suggests that in these solvents high-spin species are formed. Systematic ESR studies have shown that the orthorhombic spectra of the low-spin [Co(ORN$_3$C$_6$H$_4$X)$_2$] and [Co{(ORN$_3$C$_6$H$_4$)$_2$}] complexes observed in frozen toluene–CH$_2$Cl$_2$ solutions at 77 K[1] vanish completely or decrease considerably in their intensities upon addition of Lewis bases such as pyridine, 4-cyanopyridine, *N*-ethylimidazole, 1,2-dimethylimidazole or triphenylphosphine under anaerobic conditions. Frozen solutions of chelates with a small steric hindrance about the cobalt atom, *e.g.* [Co(OMeN$_3$C$_6$H$_4$OMe-4)$_2$], become ESR silent at a base to complex ratio as low as 1.8 : 1 for Lewis bases like pyridine or *N*-ethylimidazole. Therefore one can infer that co-ordination of monodentate ligands, leading to five-co-ordinate species, results in high-spin species exclusively. This is in contrast with what was observed for cobalt(II) complexes of tetradentate Schiff bases. Extensive NMR and ESR studies[13–17] revealed a great diversity of the behaviour of Co(salen)-type complexes [H$_2$salen = *N,N′*-ethylenebis(salicylideneimine)] in solutions of non- or weakly co-ordinating solvents, depending on the basicity of the solvents and electronic as well as steric properties of the complex. Generally, five-co-ordinate adducts of Co(salen) and its derivatives are low spin, but show temperature-dependent magnetic moments in solutions.[18,19] According to Migita *et al.*[17] the apical co-ordination of a single base molecule alone is

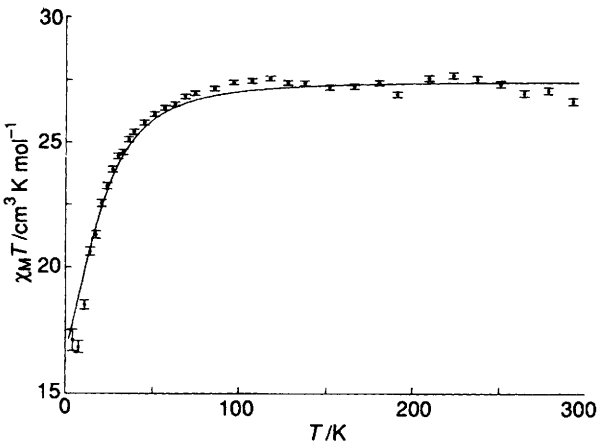

**Fig. 1** Plot of $\chi_M T$ *vs.* $T$ for [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]·C$_5$H$_5$N. The solid line was calculated according to equation (1)

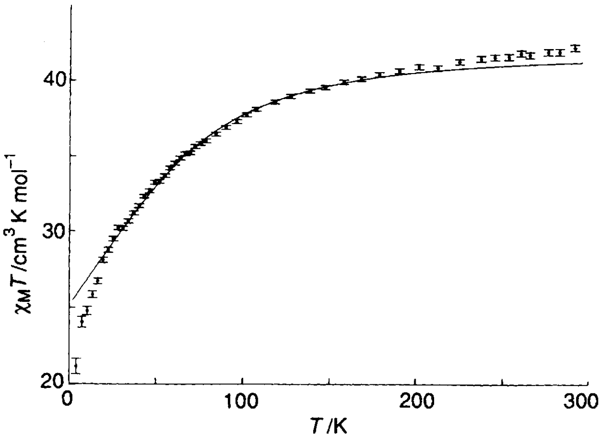

**Fig. 2** Plot of $\chi_M T$ *vs.* $T$ for [Co(OMeN$_3$C$_6$H$_4$Me-4)$_2$]·C$_3$H$_4$N$_2$. The solid line was calculated according to equation (1). The best-fit parameters are: $g$ = 2.662, $(D^2 + 3E^2)^{\frac{1}{2}}$ = 147.9 cm$^{-1}$

not capable of altering the ground-state spin multiplicity of Co(salen)-type complexes. In contrast, the co-ordination of a Lewis base to bis(bidentate Schiff base) complexes with CoN$_2$O$_2$-type chromophores results with no exception in the high-spin adducts.[20]

The analysis of magnetic susceptibility data (see SUP 56877) for the isolated solid [Co(ORN$_3$C$_6$H$_4$X)$_2$]·Lewis base complexes confirmed the conclusions drawn from frozen-solution ESR studies: all adducts are high spin with nearly constant magnetic moments of 4.1–4.3 in the range 77–300 K (see Table 1). For [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]·C$_5$H$_5$N and [Co(OMeN$_3$C$_6$H$_4$Me-4)]·C$_3$H$_4$N$_2$ the magnetic susceptibilities were determined in the range 4.2–300 K. In both cases the magnetic moments decrease continuously below 50 K reaching the values of 3.3 and 3.7 at 4.2 K, respectively.

The temperature dependence of the magnetic susceptibility of [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]·C$_5$H$_5$N was interpreted in terms of zero-field splitting of the $^4$B$_1$ ground state. According to Thuéry and Zarembowitch,[21] assuming an isotropic $g$ tensor, the $\chi_M T$ product for this case is given by equation (1) where $x = 2(D^2 + 3E^2)^{\frac{1}{2}}/kT$ and $D$ and $E$ denote the axial and rhombic components of the zero-field splitting, respectively. The temperature-independent paramagnetism was neglected. The best-fit parameters are $g$ = 2.16 and $(D^2 + 3E^2)^{\frac{1}{2}}$ = 25.3 cm$^{-1}$ (see Fig. 1). These values are typical for high-spin, five-co-ordinate cobalt(II) complexes[22] and close to those obtained by Kennedy *et al.*[9,23] for high-spin *N*-methylimidazole adducts of cobalt(II) Schiff-base complexes. On the other hand the temperature dependence of $\chi_M T$ for the imidazole adduct [Co(OMeN$_3$C$_6$H$_4$Me-4)$_2$]·C$_3$H$_4$N$_2$ could not be fitted on the basis of the above model (see Fig. 2).

$$\chi_M T = (g^2/8)\left[(9/4) + 3 \cdot \frac{1 - e^{-x}}{x(1 + e^{-x})}\right] \qquad (1)$$

**Table 2** Final positional parameters for the non-H atoms of [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]·C$_5$H$_5$N

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Co(1) | 0 | 0.244 62(7) | 0.25 |
| Co(2) | 0.5 | 0.251 03(7) | 0.25 |
| Cl(1) | −0.291 44(9) | 0.503 20(13) | −0.323 31(18) |
| Cl(2) | 0.207 09(9) | 0.023 60(14) | 0.553 07(20) |
| O(1) | 0.107 4(2) | 0.246 7(3) | 0.219 2(3) |
| O(2) | 0.608 5(2) | 0.243 0(3) | 0.385 2(4) |
| N(1) | 0.104 3(3) | 0.284 6(3) | 0.093 4(4) |
| N(2) | 0.044 2(3) | 0.319 3(3) | 0.008 1(4) |
| N(3) | −0.016 1(2) | 0.310 5(3) | 0.057 2(4) |
| N(4) | 0 | 0.076 0(5) | 0.25 |
| N(11) | 0.605 8(3) | 0.207 1(3) | 0.507 9(4) |
| N(21) | 0.544 9(3) | 0.177 1(3) | 0.535 9(4) |
| N(31) | 0.483 7(2) | 0.189 0(3) | 0.427 4(4) |
| N(41) | 0.5 | 0.419 2(5) | 0.25 |
| C(1) | −0.079 9(3) | 0.356 0(4) | −0.037 9(5) |
| C(2) | −0.075 3(3) | 0.431 1(4) | −0.140 4(5) |
| C(3) | −0.139 6(4) | 0.475 0(5) | −0.229 9(6) |
| C(4) | −0.210 1(3) | 0.445 7(4) | −0.213 8(6) |
| C(5) | −0.216 7(3) | 0.372 6(5) | −0.113 5(6) |
| C(6) | −0.151 9(3) | 0.327 5(4) | −0.026 5(5) |
| C(7) | 0.175 1(3) | 0.287 0(5) | 0.051 1(7) |
| C(8) | 0.047 2(5) | 0.021 5(5) | 0.196 9(9) |
| C(9) | 0.047 8(5) | −0.090 6(6) | 0.194 3(10) |
| C(10) | 0 | −0.145 9(7) | 0.25 |
| C(11) | 0.419 0(3) | 0.147 9(4) | 0.461 9(5) |
| C(21) | 0.423 1(3) | 0.072 6(4) | 0.566 8(5) |
| C(31) | 0.358 7(3) | 0.034 6(4) | 0.595 6(6) |
| C(41) | 0.289 2(3) | 0.072 1(4) | 0.517 4(6) |
| C(51) | 0.282 9(3) | 0.145 5(4) | 0.411 7(6) |
| C(61) | 0.348 3(3) | 0.183 4(4) | 0.384 5(5) |
| C(71) | 0.677 1(3) | 0.198 9(6) | 0.618 8(6) |
| C(81) | 0.454 6(4) | 0.474 6(5) | 0.145 2(6) |
| C(91) | 0.453 5(5) | 0.584 7(5) | 0.142 5(7) |
| C(101) | 0.5 | 0.640 1(7) | 0.25 |

It is of importance to note that although the solid 1,2-dimethylimidazole and pyridine adducts are ESR silent, the isolated imidazole adducts reveal broad, unresolved ESR spectra implying different character of the adducts of unsubstituted imidazole. Kennedy *et al.*[9] reported the peculiar properties of the [Co(salphen)]·C$_3$H$_4$N$_2$ [H$_2$salphen = *o*-phenylenebis(salicylideneimine)] adduct. For this complex the variations of magnetic moments in the low-temperature region suggested a weak antiferromagnetic coupling of a $S = \frac{1}{2}$ dimer, in contrast to that found for adducts of substituted imidazoles. The same authors have shown that for [Co(3OMe-salen)]·H$_2$O, a hydrogen-bonded dimer, both zero-field splitting and exchange effects have to be taken into account to obtain an acceptable fit of magnetic susceptibility data.[23] Thus some weak exchange interactions might be expected for imidazole adducts of cobalt(II) triazene 1-oxide chelates.

*Molecular Structure of* [Co(OMeN$_3$C$_6$H$_4$Cl-4)$_2$]·C$_5$H$_5$N.—In the crystal lattice there are two crystallographically inequivalent molecules (A and B), only slightly differing in their structures, which are placed on the two-fold axes. The atom coordinates, bond lengths and angles are listed in Tables 2 and 3. An ORTEP[24] drawing of molecule A is shown in Fig. 3.

The cobalt atoms are five-co-ordinate. Both inequivalent molecules display exact $C_2$ symmetry with Co atoms and pyridine molecules lying on the two-fold axes. The co-ordination polyhedron can be best described as a distorted trigonal bipyramid with both triazene N(3) and pyridine nitrogen atoms

**Table 3** Bond distances (Å) and angles (°) with standard deviations in parentheses *

| Molecule A | | Molecule B | |
|---|---|---|---|
| Co(1)–O(1) | 2.077(4) | Co(2)–O(2) | 2.080(3) |
| Co(1)–N(3) | 2.015(4) | Co(2)–N(31) | 2.004(4) |
| Co(1)–N(4) | 2.117(5) | Co(2)–N(41) | 2.111(5) |
| O(1)–N(1) | 1.311(5) | O(2)–N(11) | 1.301(5) |
| N(1)–N(2) | 1.270(5) | N(11)–N(21) | 1.280(5) |
| N(2)–N(3) | 1.328(5) | N(21)–N(31) | 1.334(5) |
| N(3)–C(1) | 1.409(6) | N(31)–C(11) | 1.419(5) |
| C(1)–C(2) | 1.399(6) | C(11)–C(21) | 1.386(6) |
| C(2)–C(3) | 1.384(7) | C(21)–C(31) | 1.375(8) |
| C(3)–C(4) | 1.397(8) | C(31)–C(41) | 1.384(8) |
| C(4)–C(5) | 1.376(7) | C(41)–C(51) | 1.370(7) |
| C(5)–C(6) | 1.386(7) | C(51)–C(61) | 1.385(8) |
| C(6)–C(1) | 1.405(8) | C(61)–C(11) | 1.391(7) |
| N(1)–C(7) | 1.470(7) | N(11)–C(71) | 1.465(7) |
| C(4)–Cl(1) | 1.746(6) | C(41)–Cl(2) | 1.749(6) |
| N(4)–C(8) | 1.318(8) | N(41)–C(81) | 1.333(6) |
| C(8)–C(9) | 1.408(9) | C(81)–C(91) | 1.382(8) |
| C(9)–C(10) | 1.347(9) | C(91)–C(101) | 1.358(8) |
| N(4)–Co(1)–O(1) | 90.7(2) | N(41)–Co(2)–O(2) | 92.8(2) |
| N(4)–Co(1)–N(3) | 114.2(2) | N(41)–Co(2)–N(31) | 112.9(2) |
| O(1)–Co(1)–N(3) | 76.2(2) | O(2)–Co(2)–N(31) | 76.6(2) |
| O(1)–Co(1)–O(1$^{I}$) | 178.6(2) | O(2)–Co(2)–O(2$^{II}$) | 174.4(2) |
| N(3)–Co(1)–N(3$^{I}$) | 131.5(2) | N(31)–Co(2)–N(31$^{II}$) | 134.3(2) |
| O(1)–Co(1)–N(3$^{I}$) | 103.2(2) | O(2)–Co(2)–N(31$^{II}$) | 101.2(2) |
| Co(1)–O(1)–N(1) | 109.9(3) | Co(2)–O(2)–N(11) | 109.8(3) |
| O(1)–N(1)–N(2) | 123.7(4) | O(2)–N(11)–N(21) | 123.8(4) |
| O(1)–N(1)–C(7) | 117.2(4) | O(2)–N(11)–C(71) | 117.6(4) |
| N(2)–N(1)–C(7) | 119.1(4) | N(21)–N(11)–C(71) | 118.6(4) |
| N(1)–N(2)–N(3) | 113.3(4) | N(11)–N(21)–N(31) | 113.2(4) |
| Co(1)–N(3)–N(2) | 116.8(3) | Co(2)–N(31)–N(21) | 116.6(3) |
| Co(1)–N(3)–C(1) | 132.5(3) | Co(2)–N(31)–C(11) | 132.9(3) |
| N(2)–N(3)–C(1) | 110.7(4) | N(21)–N(31)–C(11) | 110.5(4) |
| N(3)–C(1)–C(2) | 123.3(5) | N(31)–C(11)–C(21) | 123.0(4) |
| N(3)–C(1)–C(6) | 118.6(5) | N(31)–C(11)–C(61) | 118.2(4) |
| C(2)–C(1)–C(6) | 118.1(5) | C(21)–C(11)–C(61) | 118.7(4) |
| C(1)–C(2)–C(3) | 121.3(5) | C(11)–C(21)–C(31) | 120.8(5) |
| C(2)–C(3)–C(4) | 118.9(5) | C(21)–C(31)–C(41) | 119.0(5) |
| C(3)–C(4)–C(5) | 121.4(5) | C(31)–C(41)–C(51) | 121.8(5) |
| C(4)–C(5)–C(6) | 119.1(5) | C(41)–C(51)–C(61) | 118.5(5) |
| C(1)–C(6)–C(5) | 121.2(5) | C(11)–C(61)–C(51) | 121.1(5) |
| Cl(1)–C(4)–C(3) | 119.2(4) | Cl(2)–C(41)–C(31) | 119.2(4) |
| Cl(1)–C(4)–C(5) | 119.4(4) | Cl(2)–C(41)–C(51) | 119.0(4) |
| Co(1)–N(4)–C(8) | 121.3(4) | Co(2)–N(41)–C(81) | 121.4(4) |
| C(8)–N(4)–C(8$^{I}$) | 117.5(6) | C(81)–N(41)–C(81$^{II}$) | 117.1(5) |
| N(4)–C(8)–C(9) | 122.4(7) | N(41)–C(81)–C(91) | 122.6(6) |
| C(8)–C(9)–C(10) | 119.9(7) | C(81)–C(91)–C(101) | 119.6(6) |
| C(9)–C(10)–C(9$^{I}$) | 118.0(6) | C(91)–C(101)–C(91$^{II}$) | 118.4(6) |

* Superscripts refer to atomic positions relative to atoms at $x,y,z$ (no superscript): I $-x,y,\frac{1}{2}-z$: II $1-x,y,\frac{1}{2}-z$.

in the equatorial plane and the oxygen atoms occupying axial positions. The torsion angles N(2)–N(3)–C(1)–C(2) are −20.8(7) and −22.4(13)° for molecules A and B, respectively. The distortion of the co-ordination polyhedron from an ideal trigonal bipyramid concerns mainly the equatorial plane, with N(3)–Co–N(3′) being larger than the N(3)[N(3′)]–Co–N(4) angles. The non-equivalence of molecules A and B is reflected mainly by the values of the bond angles centred on the cobalt atoms (see Table 3). The overall geometry of the co-ordination polyhedron is comparable with that of all modifications of [Co(Salmhpn)][$H_2$salmhpn = *N,N′*-4-methyl-4-azaheptane-1,7-diylbis(salicylideneimine)],[25,26] a complex active towards dioxygen in solution, apart from that for the latter the azomethine nitrogen atoms are axially co-ordinated. As will be shown, the Lewis-base adducts of triazene 1-oxide complexes of $Co^{II}$ bind dioxygen reversibly. Unfortunately, this property has not been confirmed for $[Co(OMeN_3C_6H_4Cl\text{-}4)_2]\cdot C_5H_5N$ due to the very poor solubility of both the adduct and parent chelate in non-co-ordinating solvents. Nevertheless, we assume that all the dioxygen-active five-co-ordinate complexes studied possess like structures. This might easily explain the ease of formation of the high-spin species upon co-ordination of a Lewis base to a cobalt(II) triazene 1-oxide complex. The increased non-rigidity of bis(bidentate) systems as compared with Co(salen)-type complexes may facilitate a trigonal-bipyramidal structure upon co-ordination of monodentate bases. Examination of molecular framework models reveals that such a geometry should also be preferable for complexes of tetradentate $[(ORN_3C_6H_4)_2]^{2-}$ ligands.

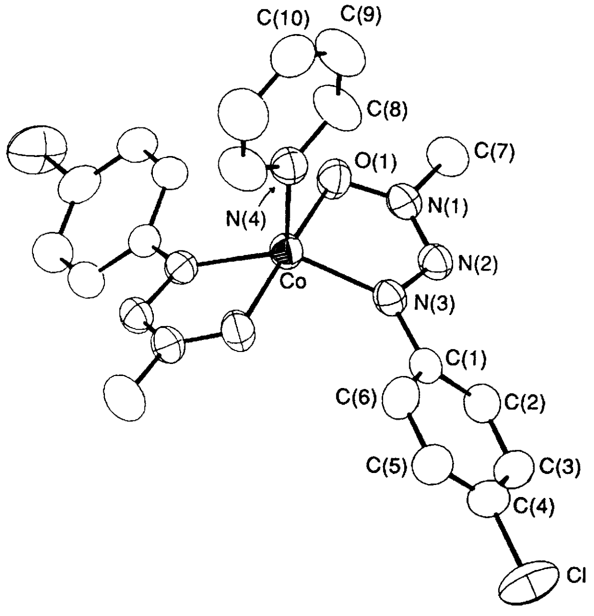

**Fig. 3** An ORTEP diagram of $[Co(OMeN_3C_6H_4Cl\text{-}4)_2]\cdot C_5H_5N$ (molecule A)

*Five-co-ordinate Adducts of Cobalt*(II) *Triazene* 1-*Oxide Complexes as Dioxygen Carriers*.—Reversible dioxygen binding was studied by means of ESR spectroscopy. About forty $[Co(ORN_3C_6H_4X)_2]$ and $[Co\{(ORN_3C_6H_4)_2\}]$ Lewis base systems were studied. As mentioned above, the addition of pyridine to $CH_2Cl_2$–toluene solutions of $[Co(ORN_3C_6H_4X)_2]$ complexes results in disappearance of ESR signals due to low-spin complexes. Passing dioxygen through those solutions at about 200 K results in most cases in ESR spectra (at 77 K) typical for cobalt superoxo complexes. After passing argon or dinitrogen through the oxygenated samples they became ESR silent. Repetition of the oxygenation/deoxygenation cycles several times (up to 70 for $[Co\{OBu^tN_3C_6H_4)_2\}]\cdot C_5H_5N$) did not produce any substantial loss of ESR signal intensities of the superoxo form at 77 K. Similar results were obtained when *N*-ethylimidazole or 4-cyanopyridine was used instead of pyridine.

The spin-Hamiltonian parameters of the superoxo complexes were obtained (Table 4) by means of computer simulation, assuming a monoclinic symmetry. The coordinate system of the Co–$O_2$ centre is depicted in Fig. 4 where α represents the angle between *A* and *g* tensors. Following the treatment given by Smith *et al.*[27] the spin-polarization terms ($f + h$) and ($g + h$) were elucidated. Representative ESR spectra of superoxo complexes are shown in Figs. 5 and 6.

All values of the *g* and *A* tensor components are comparable with those for the known cobalt(II) superoxo complexes.[4] Positive values of ($f + h$) imply an indirect spin-polarization contribution to the hyperfine structure.[4,27] The α values reflect most likely the effect of steric crowding around the Co–$O_2$ moiety: as the number of methyl substituents in *ortho* positions of the aromatic ring and the bulkiness of the R substituents increase the value of α increases reaching a maximum value of 29.5° for $[Co(OEtN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ compared

**Table 4** Spin-Hamiltonian parameters and polarization terms of selected $[Co(ORN_3C_6H_4X)_2]\cdot B\cdot O_2$ and $[Co\{(ORN_3C_6H_4)_2\}]\cdot B\cdot O_2$ complexes

| Complex | α/° | $g_x$ | $g_y$ | $g_z$ | $10^4A_x$/ cm$^{-1}$ | $10^4A_y$/ cm$^{-1}$ | $10^4A_z$/ cm$^{-1}$ | $(f+h)$ | $(g+h)$ |
|---|---|---|---|---|---|---|---|---|---|
| $[Co\{(OMeN_3C_6H_4)_2\}]\cdot C_5H_8N_2\cdot O_2$[a] | 23 | 2.010 | 2.096 | 1.992 | 7.0 | 23.0 | 11.0 | 1.7 | 15.7 |
| $[Co\{(OMeN_3C_6H_4)_2\}]\cdot C_5H_5N\cdot O_2$ | 24 | 2.010 | 2.089 | 1.991 | 7.0 | 21.0 | 10.0 | 1.7 | 14.6 |
| $[Co\{(OPr^nN_3C_6H_4)_2\}]\cdot C_5H_5N\cdot O_2$ | 24 | 2.010 | 2.089 | 1.991 | 7.0 | 21.0 | 10.0 | 1.7 | 14.6 |
| $[Co\{(OBu^tN_3C_6H_4)_2\}]\cdot C_5H_5N\cdot O_2$ | 24 | 2.010 | 2.089 | 1.991 | 7.0 | 21.0 | 10.0 | 1.7 | 14.6 |
| $[Co(OBu^tN_3Ph)_2]\cdot C_5H_5N\cdot O_2$ | 27 | 2.011 | 2.085 | 1.986 | 8.0 | 20.0 | 10.0 | 0.6 | 13.4 |
| $[Co(OBu^tN_3C_6H_4Br\text{-}4)_2]\cdot C_5H_5N\cdot O_2$ | 27 | 2.009 | 2.085 | 1.985 | 8.0 | 20.0 | 10.0 | 0.6 | 13.4 |
| $[Co(OBu^tN_3C_6H_4Me\text{-}2)_2]\cdot C_5H_5N\cdot O_2$ | 27 | 2.012 | 2.085 | 1.989 | 7.0 | 20.0 | 10.0 | 0.6 | 14.6 |
| $[Co(OBu^tN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ | 29.5 | 2.012 | 2.080 | 1.983 | 8.0 | 20.0 | 10.0 | 0.6 | 13.4 |
| $[Co(OPr^nN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ | 29.5 | 2.012 | 2.080 | 1.983 | 8.0 | 20.0 | 10.0 | 0.6 | 13.4 |
| $[Co(OEtN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ | 29.5 | 2.012 | 2.080 | 1.983 | 8.0 | 20.0 | 10.0 | 0.6 | 13.4 |
| $[Co(OPr^nN_3C_6H_4Me\text{-}2)_2]\cdot C_5H_5N\cdot O_2$ | 27 | 2.012 | 2.085 | 1.990 | 7.0 | 19.0 | 10.0 | 1.7 | 12.2 |
| $[Co(OEtN_3C_6H_4Me\text{-}2)_2]\cdot C_5H_5N\cdot O_2$ | 25 | 2.011 | 2.086 | 1.989 | 7.0 | 19.0 | 10.0 | 1.7 | 12.2 |
| $[Co(OMeN_3C_6H_4Me\text{-}2)_2]\cdot C_5H_5N\cdot O_2$ | 24 | 2.010 | 2.092 | 1.989 | 6.0 | 24.0 | 11.0 | 4.1 | 16.9 |
| $[Co(OMeN_3C_6H_4OMe\text{-}4)_2]\cdot C_5H_5N\cdot O_2$ | 25 | 2.010 | 2.087 | 1.987 | 7.0 | 20.0 | 10.0 | 0.6 | 14.6 |
| $[Co(OMeN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_6H_4N_2\cdot O_2$[c] | 23 | 2.013 | 2.093 | 1.990 | 7.0 | 23.0 | 10.0 | 1.7 | 16.9 |
| $[Co(OMeN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ | 24 | 2.014 | 2.095 | 1.992 | 7.0 | 23.0 | 10.0 | 1.7 | 16.9 |
| $[Co(OMeN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_8N_2\cdot O_2$[b] | 24 | 2.011 | 2.093 | 1.989 | 6.0 | 23.0 | 10.0 | 2.9 | 16.9 |
| $[Co(OEtN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_6H_4N_2\cdot O_2$[c] | 29.5 | 2.012 | 2.080 | 1.983 | 8.0 | 21.0 | 11.0 | 1.7 | 13.4 |

The estimated errors are: 0.001 for $g_i$, $1 \times 10^{-4}$ cm$^{-1}$ for $A_i$ and 1° for α.

[a] 1,2-Dimethylimidazole adduct. [b] 1-Ethylimidazole adduct. [c] 4-Cyanopyridine adduct.

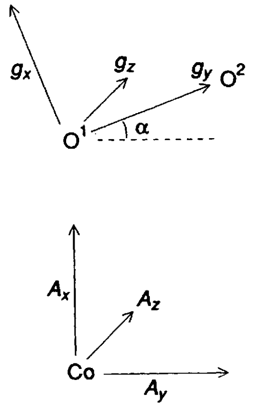

**Fig. 4** Coordinate system for a paramagnetic centre with monoclinic point group symmetry (α ≠ 0)

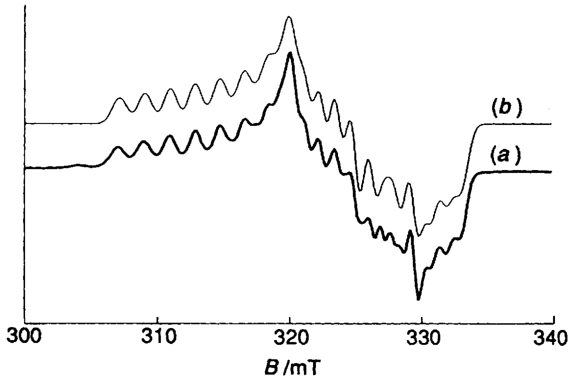

**Fig. 5** Experimental (*a*) and simulated (*b*) frozen-solution ESR X-band spectra of $[Co(OEtN_3C_6H_3Me_2\text{-}2,6)_2]\cdot C_5H_5N\cdot O_2$ in toluene–$CH_2Cl_2$ at 77 K

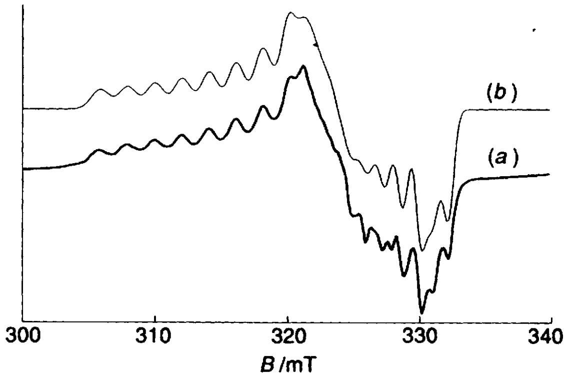

**Fig. 6** Experimental (*a*) and simulated (*b*) frozen-solution ESR X-band spectra of $[Co\{(OMeN_3C_6H_4)_2\}]\cdot C_5H_5N\cdot O_2$ in toluene–$CH_2Cl_2$ at 77 K

with α = 24° for $[Co(OMeN_3C_6H_4Me\text{-}2)_2]\cdot C_5H_5N\cdot O_2$. In terms of a model assuming monoclinic symmetry of the spin Hamiltonian, the α value is related to the Co–O(1)–O(2) angle (see Fig. 3). Indeed, the α value determined from ESR spectra of $[CoL(mim)][PF_6]_2\cdot O_2$ (L = 2,11,13,19-tetramethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene; mim = *N*-methylimidazole) is 31.5 ± 0.3°,[28] whereas X-ray studies have shown that the Co–O(1)–O(2) angle is 121 ± 1°.[29] Therefore the value of α may reflect small structural changes in superoxo complexes due to steric effects. A like relationship has been noted for dioxygen adducts of Schiff-base complexes.[4] For the present complexes the correlation between the α values and the steric crowding about the cobalt atom is quite evident for superoxo complexes derived from bis(chelate) systems.

Although the dioxygen uptake has not been measured quantitatively, the observed ESR signal intensities (at 77 K) of the oxygenated species prepared under identical conditions allowed us to distinguish three classes of four-co-ordinate triazene 1-oxide cobalt(II) chelates with regard to their ability to bind dioxygen in the presence of Lewis bases.

(*i*) Complexes derived from *o*-methyl substituted ligands *e.g.* $[Co(OMeN_3C_6H_4Me\text{-}2)_2]$, as well as complexes of tetradentate ligands such as $[Co\{(OBu^tN_3C_6H_4)_2\}]$ show well resolved ESR spectra of high intensity after oxygenation in the presence of a Lewis base. Double integration of the spectra of the parent chelates and dioxygen adducts thereof revealed that typically about 80% of the parent chelates is converted into the corresponding dioxygen adduct, *e.g.* 80% for $[Co(OEtN_3C_6H_3Me_2\text{-}2,6)_2]$ and $[Co(OBu^tN_3C_6H_3Me_2\text{-}2,6)_2]$, 90% for $[Co\{(OMeN_3C_6H_4)_2\}]$.

(*ii*) Complexes derived from ligands unsubstituted in *ortho* positions and bearing electron-releasing or slightly withdrawing substituents in *para* positions of the aromatic ring, *e.g.* $[Co(OMeN_3C_6H_4OMe\text{-}4)_2]$ or $[Co(OEtN_3C_6H_4Cl\text{-}4)_2]$, give, under identical conditions, spectra of weak or moderate

**Table 5** Charge distribution in triazene 1-oxide anions calculated by means of the INDO method[a]

| π/° | O | N(3) | N(1) | N(2) | φ[b] | $CH_3$ |
|---|---|---|---|---|---|---|
| $OMeN_3Ph^-$ | | | | | | |
| 0 | −0.605 | −0.324 | +0.187 | −0.057 | −0.199 | −0.007 |
| 15 | −0.607 | −0.324 | +0.184 | −0.057 | −0.180 | −0.016 |
| 30 | −0.609 | −0.324 | +0.178 | −0.056 | −0.170 | −0.019 |
| 45 | −0.613 | −0.323 | +0.170 | −0.056 | −0.157 | −0.022 |
| 60 | −0.616 | −0.325 | +0.164 | −0.055 | −0.143 | −0.025 |
| 75 | −0.619 | −0.326 | +0.159 | −0.054 | −0.132 | −0.028 |
| 90 | −0.619 | −0.327 | +0.157 | −0.054 | −0.146 | −0.029 |
| $OMeN_3C_6H_4NO_2\text{-}4^-$[c] | | | | | | |
| 0 | −0.585 | −0.307 | +0.213 | −0.060 | −0.253 | +0.008 |
| 90 | −0.607 | −0.325 | +0.171 | −0.049 | −0.178 | −0.012 |

[a] π Denotes the twist between the NNNO and aromatic planes given by the value of N(2)–N(3)–C(1)–C(2) torsion angle. [b] Charge on phenyl moiety. [c] The nitro group was assumed to be coplanar with the aromatic ring.

intensities as compared with chelates of class (*i*). For those complexes the integral intensities of the signal due to the superoxo complexes are less than 15% of that observed for the parent chelates, *e.g.* 5% for $[Co(OMeN_3Ph)_2]$ and $[Co(OMeN_3C_6H_4Me\text{-}3)_2]$ and 10% for $[Co(OMeN_3C_6H_4Me\text{-}4)_2]$.

(*iii*) Complexes with strong electron-withdrawing substituents in *para* positions of the aromatic rings do not bind dioxygen at all in the presence of Lewis bases. This class is represented by $[Co(OBu^tN_3C_6H_4NO_2\text{-}4)_2]$, $[Co(OPr^nN_3C_6H_4NO_2\text{-}4)_2]$ or $[Co(OMeN_3C_6H_4CO_2Et\text{-}4)_2]$.

The lack of ESR signals due to the superoxo complexes of class (*iii*) chelates results from a decrease in the ligand-field strength in the five-co-ordinate precursor. This effect is known to impair the ability of dioxygen binding.[30]

An analysis of available structural data for metal(II) triazene 1-oxide bis(chelates) indicates that the preferred dioxygen adduct formation observed for *o*-methyl-substituted $[Co(ORN_3C_6H_4X)_2]$ chelates is related to factors controlling the mutual orientation of the aromatic and $CoN_2O_2$ chelate rings. The determined values of the N(2)–N(3)–C(1)–C(2) torsion angles for the low-spin $[Co(OEtN_3Ph)_2]$,[1] high-spin $[Co(OMeN_3C_6H_4Cl\text{-}2)_2]$[31] and low-spin $[Ni(OEtN_3C_6H_4NO_2\text{-}4)_2]$[32] are 39, 29 (mean for two non-equally disposed rings) and 27.5° respectively. For the low-spin $[Co(OMeN_3C_6H_3Cl\text{-}2,Me\text{-}6)_2]$ chelate, which was shown to be isomorphic with its nickel(II) analogue,[33] owing to the steric hindrance between the 6-Me substituent and the lone pair of the N(2) atom a considerable increase in the observed torsion angles to 71 and 81° for the non-equally disposed aromatic rings is observed. Molecular framework models for square-planar complexes of tetradentate $[(ORN_3C_6H_4)_2]^{2-}$ ligands indicate that in this case the large values of the above torsion angle are inevitable as well. That such a twisted conformation is likely to influence the ligand anion basicity is supported by intermediate neglect of differential overlap (INDO) calculations of the charge distribution for different conformations of the $OMeN_3Ph^-$ anion using the CNINDO program.[34] The results, including also the effect of an electron-withdrawing nitro substituent in *para* position, are given in Table 5. It is seen that an increase in the torsion angle N(2)–N(3)–C(1)–C(2) (π) leads to an increase in charge on the NNNO moiety. An increase in the ligand-field strength resulting from increasing torsion angle becomes sufficient to stabilize the low-spin configuration of the $Co^{II}$ in $[Co(OMeN_3C_6H_3Cl\text{-}2,Me\text{-}6)_2]$ if compared with the high-spin $[Co(OMeN_3C_6H_4Cl\text{-}2)_2]$.

Although with no exception all bis(chelates) of *p*-nitro-substituted triazene 1-oxides were shown to be inactive in reversible dioxygen binding, they become active if additional methyl substituents are present in *ortho* positions of the aromatic ring. For example, in contrast to $[Co(OPr^nN_3C_6H_4NO_2\text{-}4)_2]$, its 2-Me substituted analogue $[Co(OPr^nN_3C_6H_3NO_2\text{-}4,Me\text{-}2)_2]$ becomes appreciably active towards dioxygen in the presence of stoichiometric amounts of pyridine. About 70% of the parent $[Co(OPr^nN_3C_6H_3NO_2\text{-}4,Me\text{-}2)_2]$ chelate is converted into the dioxygen adduct. This clearly shows that the *o*-methyl substitution of the ligand phenyl ring is decisive for the reactivity of five-co-ordinate Lewis-base adducts towards dioxygen.

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