NN-Dialkylcarbamato-complexes of Cobalt(II) †

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By reaction of anhydrous cobalt(II) chloride with a secondary amine and carbon dioxide in a hydrocarbon solvent, *NN*-dialkylcarbamato-complexes of cobalt(II), $[Co_n(O_2CNR_2)_{2n}]$ (R = Et or Pr^i), have been prepared. The crystal and molecular structure of the hexameric violet derivative, $[Co_6(O_2CNEt_2)_{12}]$, has been solved by *X*-ray diffraction methods. The complex is monoclinic, space group *C*2/*c*, with a = 18.428(9), b = 19.189(8), c = 24.654(13) Å, β = 95.90(6)°, Z = 8, and R = 0.0639. The six cobalt atoms are joined by bridging carbamato-groups. The main structural feature of the hexameric molecule is that four of the cobalt atoms are five-co-ordinated in a distorted trigonal bipyramidal geometry. The cobalt(II) complexes react with electrophiles with displacement of carbon dioxide.

Two preparative procedures are presently available for the synthesis of *NN*-dialkylcarbamato-complexes of transition elements, of general formula $[\{M(O_2CNR_2)_n\}_m]$: (*a*) the reaction of dialkylamido-derivatives with carbon dioxide, successfully used for the preparation of titanium(IV),[1] niobium(V), tantalum(V),[2] tungsten(III),[3] and uranium(IV)[4] complexes; and (*b*) the reaction of the metal halide with a second amine and carbon dioxide, used in these laboratories for the preparation of the lanthanide(III)[5,6] and uranium(IV)[7] derivatives. The second method of preparation does not require the preliminary preparation of the amido-complex and as such has a wider applicability. We are presently engaged in a research project dealing with the preparation of new *NN*-dialkylcarbamato-complexes of transition elements whose corresponding amido-derivatives are unstable or elusive. This paper reports the preparation of the first *NN*-dialkylcarbamato-compounds of cobalt(II) and the crystal and molecular structure of one of these.

Experimental

All manipulations and reactions involving metal complexes were carried out under an atmosphere of dry nitrogen or carbon dioxide. Infrared spectra were measured with a Perkin-Elmer model 283B instrument equipped with a grating monochromator. Magnetic susceptibilities were measured by the Faraday method using a magnetic balance calibrated with $CuSO_4\cdot5H_2O$. Solvents were carefully dried prior to use by conventional methods. The anhydrous cobalt(II) chloride used in this work was prepared according to the literature procedure[8] by treating the hydrated salt with thionyl chloride: however, we found it necessary finally to heat the chloride at about 60 °C and 10^{-2} mmHg in order to remove the lattice thionyl chloride contained in the solid.

Preparation of $[\{Co(O_2CNEt_2)_2\}_n]$.—A solution of diethylamine (11.0 cm³, 7.83 g, 107 mmol) in toluene (200 cm³) was treated with carbon dioxide at atmospheric pressure overnight. To the resulting solution, anhydrous cobalt(II) chloride (3.296 g, 25.4 mmol) was added. The resulting suspension was stirred for about 2 d at room temperature under carbon dioxide. The blue solution was filtered under carbon dioxide to eliminate most of the $[NH_2Et_2]Cl$ and the filtrate was evaporated to dryness under reduced pressure. To the resulting solid, iso-octane (100 cm³) and toluene (50 cm³) were added to eliminate the last impurities of $[NH_2Et_2]Cl$ by subsequent filtration. The filtrate was finally evaporated to dryness under reduced pressure and the blue microcrystals (yield 81%) found to be analytically pure (Found: C, 41.4; H, 7.1; N, 9.6. Calc. for $C_{10}H_{20}CoN_2O_4$: C, 41.2; H, 6.9; N, 9.6%). The compound is sensitive to moisture and is therefore stable in air only for a few minutes; it is soluble in aliphatic and aromatic hydrocarbons (the solubility in cyclohexane is 3% or higher). Reaction with dilute sulphuric acid (20%) gave quantitative evolution of carbon dioxide. Recrystallization from iso-octane gave violet crystals of the same analytical composition. Magnetic susceptibility at room temperature: $\chi_{Co}^{corr} = 9\,656 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -151×10^{-6} c.g.s.u.), corresponding to $\mu_{eff.}$ = 4.80 B.M. By cryoscopy in cyclohexane, the following values of molecular weight were found [metal concentrations (mol kg⁻¹) and multiples of the $Co(O_2CNEt_2)_2$ unit are given in parentheses]: 1 520 (0.103, 5.2); 856 (0.033, 2.9). By sublimation at 180 °C and *ca.* 10^{-3} mmHg, blue microcrystals were obtained which had a stability in air much lower than that of the starting violet solid. No reproducible analytical results could be obtained for this compound, although the i.r. spectrum in the 1 800—1 300 cm⁻¹ region indicated that it was a carbamato-complex.

Preparation of $[\{Co(O_2CNPr^i_2)_2\}_n]$.—This compound was prepared as a blue microcrystalline powder by similarly treating anhydrous cobalt(II) chloride (2.80 g, 21.6 mmol) with a solution of di-isopropylamine (12.7 cm³, 9.14 g, 90.36 mmol) in toluene (100 cm³) for 15 h at room temperature under carbon dioxide at atmospheric pressure. The resulting blue solution was filtered and then evaporated to dryness under reduced pressure and the solid residue (yield 20%) analyzed (Found: C, 48.0; H, 8.4. Calc. for $C_{14}H_{28}CoN_2O_4$: C, 48.4; H, 8.1). Magnetic susceptibility at room temperature: $\chi_{Co}^{corr} = 7\,834 \times 10^{-6}$ c.g.s.u. (diamagnetic correction = -210×10^{-6} c.g.s.u.), corresponding to $\mu_{eff.}$ = 4.30 B.M.

The cobalt(II) complexes showed the typical reactivity towards electrophilic reagents already observed[5-7] for other *NN*-dialkylcarbamato-complexes. The *NN*-diethylcarbamato-

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† *Supplementary data available* (No. SUP 23817, 13 pp.): structure factors, thermal parameters, complete set of calculated structural parameters, ligand geometries, i.r. data for selected *NN*-dialkylcarbamato-complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: mmHg ≈ 13.6 × 9.8 Pa, B.M. = 0.927 × 10^{-23} A m², $\chi_{c.g.s.u.} = \chi_{S.I.} \times 4\pi \times 10^{-6}$.

Table 1. I.r. spectra in the 1 800—1 300 cm^{-1} region and electronic spectra of *NN*-dialkylcarbamato-complexes of cobalt(II) [a]

Compound	Medium	$\tilde{\nu}$/cm^{-1}									$\lambda_{max.}$/nm [b]
$[Co(O_2CNEt_2)_2]$	C_2Cl_4	1 590w	1 550m	1 505s	1 485 (sh)	1 460m	1 430m	(−)	(−)	1 315s	554, 596, 623 (0.0023)
	C_6H_{12} [c]	1 590	1 550	(−)	(−)	(−)	(−)	1 370m	(−)	1 315s	
	thf		1 550m	(−)	(−)	(−)	(−)	(−)		1 315s	496, 554 (sh), 599 (0.023)
	$(C_2ClF_3)_n$ [d]	1 590m		1 520s	1 480s	1 455m	1 420s	1 370m	1 340m	1 310s	495, 590 (0.026)
	Nujol [d]	1 596s		1 520s	1 480s	(−)	1 430s	(−)	1 345m	1 312s	
$[Co(O_2CNPr^i_2)_2]$	C_2Cl_4		1 565s	1 515m	1 480s		1 455s	1 385m	(−)		
	C_6H_{12}		1 560m	(−)	(−)	(−)	(−)	1 385m	(−)		
	$(C_2ClF_3)_n$		1 570s	1 520m	1 480s	1 450s			1 355s		
	Nujol		1 570s	1 520m	1 480s	(−)		(−)	1 355s		

[a] Region covered by solvent absorption is denoted by (−). [b] Cyclohexane as solvent, molar concentration (mol dm^{-3}) in parentheses. [c] The relative intensities of the bands at 1 590 and 1 550 cm^{-1} are affected by concentration. Approximate ratios of absorbance (metal concentrations in parentheses) are: 0.47 (7.9 × 10^{-3}); 0.55 (15.8 × 10^{-3}); 0.73 (26 × 10^{-3}); 1.95 (79 × 10^{-3} mol dm^{-3}), with the intensity of the band at 1 590 cm^{-1} increasing with concentration. [d] Recrystallized from iso-octane.

Table 2. Non-hydrogen atomic co-ordinates (× 10^4) for $[Co_6(O_2CNEt_2)_{12}]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co(1)	−403(2)	2 757(2)	8 308(1)	C(7)	−2 400(24)	3 254(23)	9 264(19)
Co(2)	383(2)	1 315(2)	8 112(1)	C(8A)	−2 999(41)	2 925(36)	9 053(28)
Co(3)	−786(2)	4 189(2)	7 703(1)	C(8B)	−2 154(43)	3 541(42)	9 701(34)
O(1)	−38(9)	2 390(8)	9 051(6)	C(9)	−2 854(21)	4 360(21)	8 693(16)
O(2)	526(8)	1 355(9)	8 916(6)	C(10)	−2 505(22)	4 911(23)	8 990(18)
O(3)	−1 277(8)	3 135(9)	8 649(6)	C(11)	−1 072(14)	2 769(13)	7 148(10)
O(4)	−1 568(9)	4 156(9)	8 197(7)	C(12)	−1 923(20)	2 446(19)	6 331(16)
O(5)	−604(7)	2 413(7)	6 915(5)	C(13A)	−2 003(29)	2 773(28)	5 885(24)
O(6)	−933(7)	3 095(7)	7 583(6)	C(13B)	−2 386(38)	2 005(37)	6 291(27)
O(7)	665(8)	1 696(7)	6 947(6)	C(14)	−2 339(13)	3 203(13)	7 116(10)
O(8)	1 231(9)	1 194(8)	7 698(7)	C(15)	−2 663(15)	2 742(16)	7 525(12)
O(9)	−20(8)	3 808(8)	6 741(6)	C(16)	1 206(15)	1 355(14)	7 224(12)
O(10)	−1 051(8)	4 310(8)	6 915(6)	C(17)	2 434(18)	874(18)	7 195(13)
O(11)	48(10)	338(9)	7 960(8)	C(18)	2 241(19)	150(19)	7 181(15)
O(12)	−405(9)	5 172(9)	7 797(7)	C(19)	1 747(15)	1 361(15)	6 304(12)
N(1)	431(13)	1 695(14)	9 779(11)	C(20)	1 338(17)	762(17)	5 990(12)
N(2)	−2 238(14)	3 820(13)	8 855(10)	C(21)	−617(15)	4 155(14)	6 588(11)
N(3)	−1 767(12)	2 741(11)	6 885(9)	C(22)	−162(16)	4 173(15)	5 649(12)
N(4)	1 734(12)	1 178(10)	6 891(9)	C(23)	392(16)	4 743(15)	5 717(12)
N(5)	−752(12)	4 304(11)	6 057(9)	C(24)	−1 497(17)	4 629(18)	5 831(12)
N(6)	0(0)	−704(21)	7 500(0)	C(25)	−1 333(23)	5 366(23)	5 880(17)
N(7)	0(0)	6 233(22)	7 500(0)	C(26)	0(0)	12(27)	7 500(0)
C(1)	288(15)	1 837(16)	9 221(12)	C(27)	−172(18)	−1 079(15)	6 948(13)
C(2)	669(22)	943(19)	9 970(15)	C(28)	553(20)	1 179(18)	6 760(14)
C(3)	1 405(27)	1 132(24)	10 078(18)	C(29)	0(0)	5 502(26)	7 500(0)
C(4)	253(20)	2 323(19)	10 156(15)	C(30)	−566(18)	6 555(16)	7 795(13)
C(5)	−495(29)	2 151(26)	10 242(20)	C(31)	190(20)	6 678(19)	8 342(16)
C(6)	−1 636(14)	3 676(15)	8 549(10)				

derivative (1.21 g, 4.16 mmol) was reacted at room temperature with neat methyl iodide (10 cm^3) for 4 d: the solution slowly turned from blue to green while a green solid separated out which was collected by filtration and dried *in vacuo* (yield 83%) {Found: C, 18.6; H, 4.2; N, 3.1. Calc. for $[NMe_2Et_2]_2[CoI_4]$, $C_{12}H_{32}CoI_4N_2$: C, 18.7; H, 4.2; N, 3.6%}. Magnetic susceptibility at room temperature: χ_{Co}^{corr} = 10 073 × 10^{-6} c.g.s.u. (diamagnetic correction = −344 × 10^{-6} c.g.s.u.), corresponding to $\mu_{eff.}$ = 4.86 B.M.

X-Ray Crystal Structure of $[Co_6(O_2CNEt_2)_{12}]$.—*X-Ray data collection and reduction.* The violet crystals of the ethyl derivative used for the *X*-ray structural study were obtained by recrystallization from iso-octane by dissolution at the reflux temperature and by slowly cooling the solution to room temperature. Preliminary crystal examination and subsequent data collection were performed on an on-line single-crystal Siemens AED diffractomer, with the use of niobium-filtered Mo-K_α radiation (λ = 0.710 69 Å). A suitable crystal was sealed in a Lindemann capillary and then mounted in an arbitrary direction. Peak search, centring, and indexing computer programs were used to determine the crystal system and approximate lattice parameters. Precise unit-cell dimensions and their standard deviations were derived by least-squares refinement of the setting angles of 17 computer centred reflections.

Crystal Data.—$C_{30}H_{60}Co_3N_6O_{12}$ (for half of the hexameric unit), *M* = 873.64, monoclinic, *a* = 18.428(9), *b* = 19.189(8), *c* = 24.654(13) Å, β = 95.90(6)°, *U* = 8 672(7) Å^3, *Z* = 8, D_c = 1.338 g cm^{-3}, *F*(000) = 3 672, μ(Mo-K_α) = 11.88 cm^{-1}.

Intensity data were recorded at room temperature with θ in the range 3.0—24.0°, using the θ–2θ scan method and a variable scan rate of 2.5—10.0° min^{-1}. The pulse-height discriminator was set to accept 90% of the Mo-K_α peak. All the reflections in the quadrant $\pm h + k + l$ were collected, excluding those with $h + k$ odd. In this way, a total of 5 888 reflections were measured, 5 719 of them being unique; of these, 1 258, having $I > 2\sigma(I)$, were used in the subsequent calculations. Two check reflections ($\bar{3}$ 3 7 and 3 1 7), monitored every 75 reflections, gave no indication of crystal decay or loss of alignment. Systematic absences were found to be $h\,k\,l$ with $h + k$ odd and $h\,0\,l$ with l odd, consistent with the space group $C2/c$ or Cc; the former was proved to be correct by the successful refinement of the structure. Due to the irregular shape of the crystal and to the low value of μ, no absorption corrections were applied. The data were therefore corrected only for Lorentz and polarization effects.

Structure Determination and Refinement.—The positions of the three independent cobalt atoms were determined by multi-solution Σ_2 sign expansion and all the remaining non-hydrogen atoms were located by a series of refinements and subsequent electron-density difference syntheses. From a difference-Fourier map, two of the ethyl groups, one bonded to N(2) and the other to N(3), were found to be oriented in two different ways with a statistical distribution limited to the terminal carbon atoms. Refinement was carried out by full-matrix least squares, minimizing $\Sigma w|\Delta F^2|$. Because of the relatively few data with $I > 2\sigma(I)$, anisotropic motion was considered for the cobalt atoms only, while isotropic thermal parameters were used for the other atoms. Individual weights were ascribed according to the scheme $w = k/\sigma^2(F_0) + g|F_0|^2$ where the final k and g values were 0.4814 and 0.004 85, respectively. The final values of the residuals were $R = 0.0639$ and $R' = 0.0648$. A final difference-Fourier map was featureless. Scattering factors for neutral atoms were taken from ref. 9. Corrections for the real and imaginary parts of the anomalous dispersion were applied to cobalt.[10] All computations were carried out on the Cyber 76 computer of CINECA (Casalecchio, Bologna) with the SHELX 76 system of programs.[11] The final atomic co-ordinates are given in Table 2 and the relevant bond distances and angles in Table 3.

Results and Discussion

The *NN*-dialkylcarbamato-complexes of cobalt(II) have been prepared by a method well established in earlier papers,[5–7] namely by reacting the anhydrous metal chloride with the secondary amine and CO_2 in a hydrocarbon solvent [equation (i)]. In view of its elevated solubility in the hydrocarbon, the

$$\mathrm{CoCl_2 + 4NHR_2 + 2CO_2 \longrightarrow 2[NH_2R_2]Cl + [Co(O_2CNR_2)_2]} \quad \text{(i)}$$

cobalt complex was recovered from the reaction mixture by filtering off the sparingly soluble dialkylammonium chloride.

With regard to the complex bonding arrangements possible for *NN*-dialkylcarbamato-complexes, as indicated by earlier work on this subject,[5,6,12,13] and of the low diagnostic value of i.r. spectroscopic data for bonding assignments, it was decided to carry out an *X*-ray diffraction study of one of the compounds prepared.

The molecular structure of the ethyl derivative consists of discrete $[Co_6(O_2CNEt_2)_{12}]$ units, with no relevant intermolecular interactions. A view of the hexameric unit is shown in Figure 1, which also shows the numbering system used. The cobalt atoms are arranged at the corners of a puckered six-membered ring with cobalt–cobalt distances ranging from 3.161(5) to 3.197(4) Å (see Table 3). The structure contains three crystallographically independent cobalt atoms in the asymmetric unit. The primed atoms are related to the other half of the hexameric unit by a two-fold rotation axis.

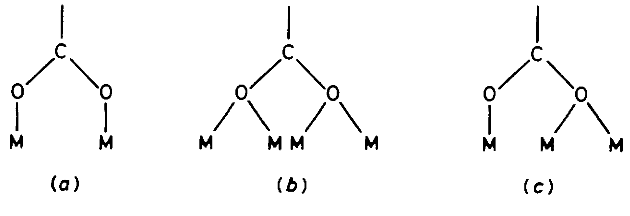
Table 3. Bond distances (Å) and angles (°) in the three co-ordination polyhedra of $[Co_6(O_2CNEt_2)_{12}]$

Co(1)–O(1)	2.01(1)	Co(2)–O(5′)	2.15(1)
Co(1)–O(3)	2.03(2)	Co(2)–O(7′)	2.06(1)
Co(1)–O(6)	2.05(1)	Co(1) ··· Co(2)	3.183(6)
Co(1)–O(5′)	2.10(1)	Co(3) ··· Co(3′)	3.161(5)
Co(1)–O(7′)	2.17(1)	Co(3)–O(4)	1.98(2)
Co(1)–O(9′)	2.17(2)	Co(3)–O(6)	2.13(1)
Co(2) ··· Co(2′)	3.197(4)	Co(3)–O(10)	1.97(1)
Co(2)–O(2)	1.97(1)	Co(3)–O(12)	2.02(2)
Co(2)–O(8)	1.97(2)	Co(3)–O(9′)	2.05(1)
Co(2)–O(11)	2.00(2)	Co(1) ··· Co(3)	3.171(5)

O(1)–Co(1)–O(3)	87.3(6)	O(2)–Co(2)–O(7′)	94.9(6)
O(1)–Co(1)–O(6)	171.1(6)	O(8)–Co(2)–O(11)	92.2(7)
O(1)–Co(1)–O(5′)	84.6(6)	O(8)–Co(2)–O(5′)	86.3(6)
O(1)–Co(1)–O(7′)	88.8(6)	O(8)–Co(2)–O(7′)	142.8(6)
O(1)–Co(1)–O(9′)	106.7(6)	O(11)–Co(2)–O(5′)	166.1(7)
O(3)–Co(1)–O(6)	85.5(6)	O(11)–Co(2)–O(7′)	92.9(7)
O(3)–Co(1)–O(5′)	170.0(6)	O(5′)–Co(2)–O(7′)	80.1(5)
O(3)–Co(1)–O(7′)	107.1(6)	O(4)–Co(3)–O(6)	87.9(6)
O(3)–Co(1)–O(9′)	89.8(6)	O(4)–Co(3)–O(10)	119.2(7)
O(6)–Co(1)–O(5′)	103.1(5)	O(4)–Co(3)–O(12)	103.0(7)
O(6)–Co(1)–O(7′)	88.4(5)	O(4)–Co(3)–O(9′)	95.8(7)
O(6)–Co(1)–O(9′)	78.4(6)	O(6)–Co(3)–O(10)	87.9(6)
O(5′)–Co(1)–O(7′)	78.8(5)	O(6)–Co(3)–O(12)	166.8(6)
O(5′)–Co(1)–O(9′)	86.9(6)	O(6)–Co(3)–O(9′)	79.3(6)
O(7′)–Co(1)–O(9′)	157.8(6)	O(10)–Co(3)–O(12)	92.9(7)
O(2)–Co(2)–O(8)	119.6(7)	O(10)–Co(3)–O(9′)	142.3(6)
O(2)–Co(2)–O(11)	103.4(7)	O(12)–Co(3)–O(9′)	92.1(7)
O(2)–Co(2)–O(5′)	89.2(6)		

Primed atoms indicate the symmetry operation $-x, y, \frac{3}{2} - z$.

There are seven crystallographically independent ligand groups in the asymmetric unit; five are in general positions, while two occupy a special position of the space group $C2/c$, with the N and the sp^2 C atoms being situated in a crystallographic two-fold axis. Of particular interest is the bonding arrangement of the carbamato-ligands. The hexameric unit is held together by bridging ligands of three different types (*a*)—(*c*). There are eight carbamato-ligands of type (*a*), two of type (*b*), and four of type (*c*). An interesting feature of the structure is the presence of two types of cobalt atoms, a six-co-ordinated cobalt [Co(1)] located at the centre of Figure 1 and two external five-co-ordinated cobalts [Co(2) and Co(3)]. Each of Co(2) and Co(3) is connected to Co(1) by bridging oxygen atoms of the carbamato-ligands, one at an equatorial and the other at an axial site of a distorted trigonal bipyramid. This is shown in the perspective view of Figure 2 which displays the ellipsoids of thermal motion. The co-ordination geometry around Co(1) is that of a distorted octahedron, the six-co-ordination sites being occupied by oxygen atoms from different carbamato-groups: two of type (*a*), two of type (*b*), and two of type (*c*). Accordingly three kinds of Co(1)—O distances are observed, their values increasing in the sequence: (*a*) 2.02 (av.) < (*b*) 2.07 (av.) < (*c*) 2.17 (av.) Å. These dif-



(*a*) (*b*) (*c*)

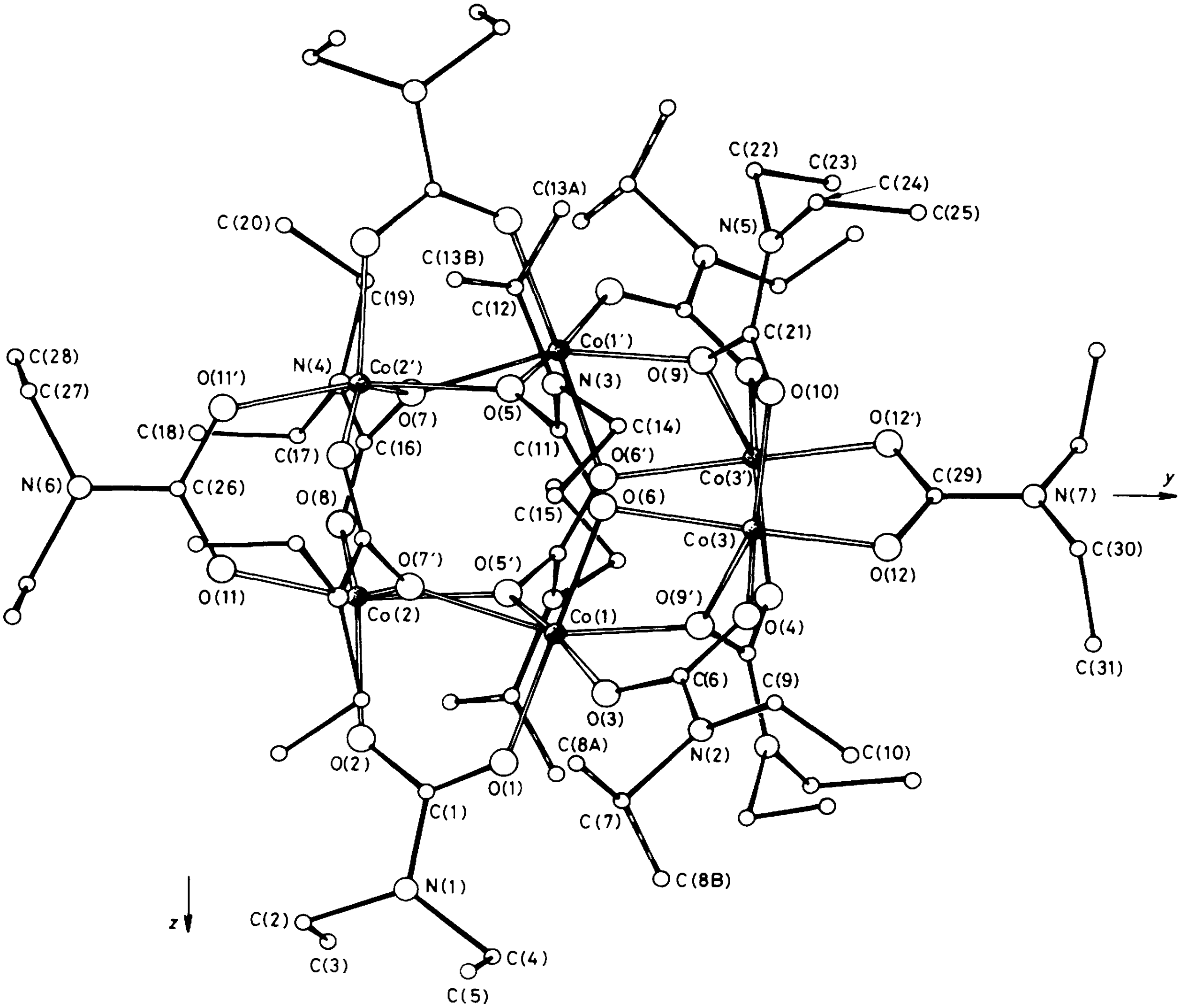


Figure 1. Structure of the hexamer [Co$_6${O$_2$CNEt$_2$}$_{12}$], viewed along the *a* axis. Primed atoms are related to the corresponding unprimed ones by a two-fold axis of rotation

ferences are also reflected in distortions of the polyhedral geometry about the metal. The greatest deviation from octahedral geometry is the O(7′)–Co(1)–O(9′) angle which is 157.8(6)°. The other two *trans* bond angles are 170.0(6) and 171.1(6)°, while the *cis* angles range from 78.4(6) to 107.1(6)°.

The Co–O type (*a*) and Co–O type (*b*) distances appear to be in accord with those usually found in octahedral cobalt(II) complexes,[14] while for the Co–O type (*c*) distances, a direct comparison can be made with the 'long' bonds observed in octahedral complexes showing a similar large spread in the Co–O bond distances.[15]

The Co(2) and Co(3) atoms with a geometry resembling a distorted trigonal bipyramid have identical sets of ligands, as mentioned above. In each case, the basal plane, consisting of one type (*a*) and two type (*c*) atoms, is somewhat distorted with bond angles ranging from 94.9 to 142.8°, instead of the ideal 120° angle; the axial angle is considerably smaller than the ideal value of 180°. Both polyhedra have one of the axial Co–O distances rather longer than the remaining four, the distance being that involving the type (*b*) oxygen atom. In view of the fact that crystallographically established complexes of cobalt(II) five-co-ordinated to oxygen-containing ligands are scarce,[16,17] only a limited comparison of the data can be made. The Co(2)–O and Co(3)–O distances are in good agreement with those observed in the trigonal bipyramidal 2-methylpyridine *N*-oxide derivative, [Co{C$_5$H$_4$N(O)(Me-2)}$_5$][ClO$_4$]$_2$.[18]

Bond distances for the seven unique carbamato-ligands are not significantly different from one another [see Supplementary data: average values are C–O, 1.27(3); C$\overset{...}{-}$N, 1.39(4); C–N, 1.54(4) Å] and are generally close to those observed for other *NN*-dialkylcarbamato-complexes of transition metals studied earlier by *X*-ray diffraction methods.[2,3,5,6,12,13] With reference to the C–O bond distances within each type of carbamato-ligand, however, it can be noted that for those of type (*a*), the values range from 1.24(3) to 1.30(3) Å; ligands (*c*) have two significantly different C–O bond distances, namely 1.21(3) Å for C(16)–O(8) and 1.23(3) Å for C(21)–O(10), to be compared with 1.32(3) and 1.31(3) Å, respectively, for C(16)–O(7) and C(21)–O(9), in agreement with the non-bridging nature of the O(8) and O(10) oxygen atoms, and with the corresponding higher electron transfer to the metal. Finally, ligands of type (*b*) have C–O bond distances of 1.25(3) and 1.28(3) Å. The atoms of the O$_2$CN groups are approximately coplanar with

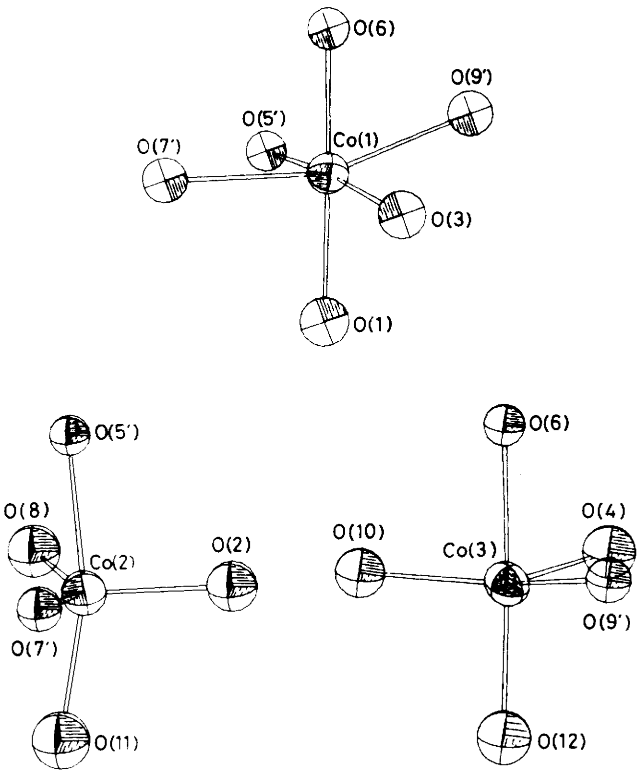


Figure 2. Perspective drawings of the three co-ordination polyhedra. The ellipsoidal boundaries are at the 30% probability level

a maximum deviation of 0.25 Å. The packing of the molecules shows no unusual features, no intermolecular contacts less than 3.40 Å being observed.

The magnetic moments of 4.80 and 4.30 B.M. for the ethyl and isopropyl derivatives respectively are, to a first approximation, in agreement with the presence of magnetically non-diluted octahedral cobalt(II) centres in the molecule [19] and of *O*-co-ordinated trigonal bipyramidal cobalt(II), such as the five-co-ordinate complex of 2-methylpyridine *N*-oxide ($\mu_{eff.}$ = 4.58 B.M. at 20 °C [20]). The rather drastic decrease of magnetic moment from the ethyl to the isopropyl derivative indicates a change of molecular geometry. This is also suggested by the somewhat different i.r. spectra (see Table 1) of the two compounds. A systematic study of the influence of the alkyl group R on the structural, spectroscopic, and magnetic properties of $[\{Co(O_2CNR_2)_2\}_n]$ complexes is now in progress and will be reported in a subsequent paper. With reference to the ethyl derivative only, the magnetic moment of 4.80 B.M. is considerably higher than that found (4.11 B.M. at 20 °C [21]) for the dimeric complex [22] tetra-μ-benzoato-bis(quinoline)dicobalt(II). This is consistent with the shorter cobalt–cobalt distance (2.832 Å) observed, as compared with that in our compound [3.178(5) (av.) Å]. Magnetic susceptibility measurements at different temperatures are necessary in order to evaluate quantitatively the amount of magnetic exchange among the cobalt(II) centres.

The types of bonding arrangements encountered until now for *NN*-dialkylcarbamato-complexes of transition elements (d^n and f^n) are (1)—(6) shown below; (3), (4), and (6) being those found in the present cobalt(II) derivative.

The complexes reported in this paper have a complicated behaviour in solution and we believe that the structure determined in the solid state is only one of the possible molecular arrangements in a non-condensed phase. This is substantiated by the following facts. (*a*) The violet crystals of the ethyl derivative have been obtained by recrystallization from boiling iso-octane and by slow cooling of the resulting solution. (*b*) Both the ethyl and the isopropyl derivatives, when prepared by evaporation to dryness of the crude reaction mixture at room temperature, are blue. The absorption spectra of their blue solutions in cyclohexane, toluene, and tetrahydrofuran (thf) change with concentration as far as both $\lambda_{max.}$ and intensity are concerned, see Figure 3. (*c*) The i.r. spectra change with concentration, see Table 1, in the significant region of the carbamato-group vibrations. (*d*) Molecular weights determined by cryoscopy in cyclohexane change with concentration.

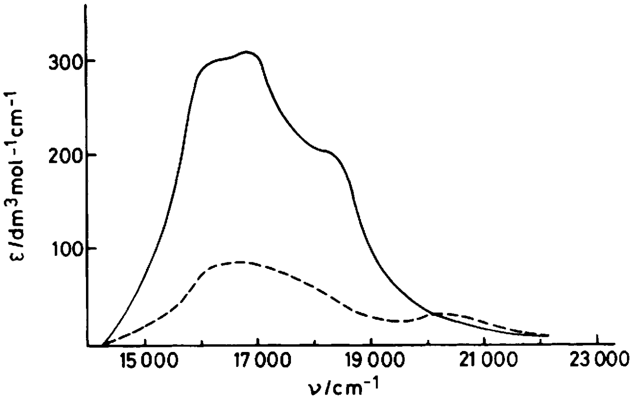
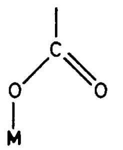
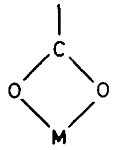


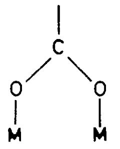
Figure 3. Absorption spectra of $[Co(O_2CNEt_2)_2]$ at different concentrations (solvent = cyclohexane): 0.002 mol dm^{-3} (——); 0.023 mol dm^{-3} (— — —)



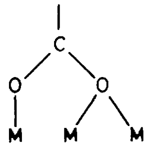
(1)



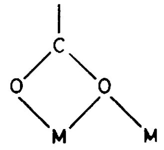
(2)



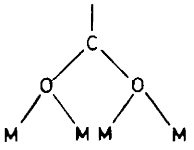
(3)



(4)



(5)



(6)

The ethyl derivative sublimes under rather drastic conditions *in vacuo* to give a blue solid, which certainly represents a different structural arrangement. The sublimed product is being investigated presently.

The visible absorption spectra of solutions obtained from the violet crystals, see Table 1 and Figure 3, are not inconsistent with the presence of six-co-ordinated [23] and five-co-ordinated [20,24] cobalt(II) in solution. The presence of substantial amounts of tetrahedral cobalt(II), in spite of the blue colour, is excluded by the absence of bands above 650 nm (below 15 000 cm^{-1}). The blue colour must therefore arise from the tail of higher frequency bands.

The cobalt(II) carbamato-complexes are reactive towards electrophilic reagents such as protons (dry hydrogen sulphide and aqueous sulphuric acid) and methyl iodide. In the latter case the tetra-iodocobaltate(II) anion was obtained [equation (ii)].

$$[Co(O_2CNEt_2)_2] + 4MeI \longrightarrow 2CO_2 + [NMe_2Et_2]_2[CoI_4] \quad \text{(ii)}$$

In view of the elevated solubility of these cobalt(II) complexes in hydrocarbons, they can be used as hydrophobic vehicles of cobalt.

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References

1 G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc. A*, 1970, 2550.

2 M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 782.

3 M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, 1977, **16**, 603.

4 K. W. Bagnall and E. Yanir, *J. Inorg. Nucl. Chem.*, 1974, **36**, 777.

5 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1979, 1103.

6 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, and G. Perego, *J. Chem. Soc., Dalton Trans.*, 1983, 483.

7 F. Calderazzo, G. Dell'Amico, R. Netti, and M. Pasquali, *Inorg. Chem.*, 1978, **17**, 471.

8 J. B. Reed, B. S. Hopkins, and L. F. Audrieth, *Inorg. Synth.*, 1939, **1**, 28.

9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101.

10 Ref. 9, pp. 149—150.

11 G. M. Sheldrick, SHELX 76, A program for crystal structure determination, University of Cambridge, 1976.

12 F. Calderazzo, G. Dell'Amico, M. Pasquali, and G. Perego, *Inorg. Chem.*, 1978, **17**, 474.

13 M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, 1978, **17**, 3536; M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, 1974, **96**, 6214; 1975, **97**, 1623; M. H. Chisholm, F. A. Cotton, and M. W. Extine, *Inorg. Chem.*, 1978, **17**, 2000; M. H. Chisholm, L. S. Tang, and J. C. Huffman, *J. Am. Chem. Soc.*, 1982, **104**, 4879.

14 G. Albertin, E. Bordignon, A. Orio, G. Pelizzi, and P. Tarasconi, *Inorg. Chem.*, 1981, **20**, 2862 and refs. therein.

15 F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 1963, **85**, 2402; F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 1145; A. G. Nord and T. Stefanidis, *Cryst. Struct. Commun.*, 1980, **10**, 1251; A. M. G. Dias Rodrigues, R. H. P. Francisco, and J. R. Lechat, *Cryst. Struct. Commun.*, 1982, **11**, 847.

16 P. L. Orioli, *Coord. Chem. Rev.*, 1971, **6**, 285.

17 B. F. Hoskins and F. D. Whillans, *Coord. Chem. Rev.*, 1972—1973, **9**, 365.

18 B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 767.

19 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 37.

20 W. Byers, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, 1968, **7**, 1835.

21 J. Drew, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 52.

22 J. Catterick, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1977, 223.

23 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., J. Wiley, New York, 1980, pp. 770—773.

24 M. Ciampolini, *Struct. Bonding* (*Berlin*), 1969, **6**, 52.

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