trans-Azido(dimethylglyoximato-N,N')(dimethylglyoxime-N,N')(pyridine)cobalt(III),*
[Co(C₅H₅N)(C₄H₆N₂O₂)(C₄H₈N₂O₂)N₃]

BY M. N. PONNUSWAMY AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Abstract. $M_r = 410.3$, $F(000) = 848$, monoclinic, $P2_1/n$, $a = 8.739$ (2), $b = 13.990$ (2), $c = 14.519$ (3) Å, $\beta = 98.11$ (2)°, $V = 1757.3$ (5) Å³, $Z = 4$, $D_m = 1.558$, $D_x = 1.547$ Mgm⁻³, μ (Mo $K\alpha$) = 8.9 cm⁻¹, $\lambda = 0.71073$ Å, $T = 294$ K. The structure was determined from CAD-4 diffractometer data by Patterson and Fourier syntheses, and refined by least-squares methods to $R = 0.030$ for 3307 reflections. Co is coordinated octahedrally to the N atoms of dmg (and H₂dmg) ligands, the azide, and pyridine groups; Co—N = 1.895 (2) (dmg), 1.950 (2) (azide), 1.973 (1) Å (pyridine). The azide group is slightly asymmetric and non-linear, N—N = 1.177 (2), 1.146 (3) Å, N—N—N = 174.8 (2)°.

Introduction. In recent years the chemistry of cobaloximes has been given considerable attention since these materials have been used as model compounds (Schrauzer, 1968) for vitamin B₁₂. A study of an azidocobaloxime (Vijayaraghavan, Thillaichidambaram, Raghavan & Santappa, 1978) is of interest in view of the behaviour of the azide group and pyridyl moiety coordinated to the metal atom. Herein we report the crystal and molecular structure of *trans*-azido(dimethylglyoximato-N,N')(dimethylglyoxime-N,N')(pyridine)cobalt(III).

Experimental. Red crystals (from ethanol); $0.2 \times 0.4 \times 0.6$ mm; CAD-4 diffractometer; graphite-monochromatized Mo $K\alpha$; hkl with $\theta \leq 30.0°$; ω–2θ scan; ω-scan width $(0.60 + 0.35 \tan \theta)°$ extended 25% on each side for background measurement; horizontal aperture $(2.0 + \tan \theta)$ mm; vertical aperture 4 mm; cell parameters from least-squares fit of sin θ values for 25 reflections with $15 < \theta < 23°$; $\leq \pm 0.8\%$ deviation for three reference reflections monitored each hour; 5111 independent reflections; 3307 (64.7%) with $I \geq 3 \sigma (I)$ where $\sigma^2(I) = S + 2B + [0.04 (S-B)]^2$; S = total peak count and B = time-averaged background; Lp corrections and absorption correction (transmission factors ranged from 0.769 to 0.862, Coppens, Leiserowitz & Rabinovich, 1965; Busing & Levy, 1967); structure solved by heavy-atom and Fourier methods; full-matrix

least-squares [$\sum w(\Delta F)^2$ minimized] with anisotropic thermal parameters, H atoms from a difference synthesis, isotropic type; subsequent refinement included anomalous scattering; final $R = 0.030$, $R_w = 0.038$ for 311 variables; $R = 0.063$ for all data; $w = 1/\sigma^2$ (F); mean and maximum parameter shifts 0.11σ and $0.98\,\sigma$, respectively; standard deviation in an observation of unit weight 1.70; $\pm$ 0.42 e Å⁻³ in the final difference synthesis; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965); anomalous-scattering factors from Cromer & Liberman (1970); local adaptations of standard computer programs, *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *FORDAP* (A. Zalkin unpublished) and *ORTEP* II (Johnson, 1976).

Discussion. Final atomic coordinates are given in Table 1.†

A stereodiagram of the molecule and a projection showing the crystallographic numbering scheme are shown in Fig. 1. The thermal motion has been analysed in terms of the rigid-body modes of translation, libration and screw motion (Schomaker & Trueblood, 1968). The r.m.s. error in the temperature factors $\sigma(U_{ij})$ derived from least-squares analysis is 0.0015 Å². The molecule does not behave as a single rigid body; however, three groups, consisting of the cobalt taken together with each of the dimethylglyoxime ligands and the pyridine ligand, behave as rigid bodies. The segments of the molecule were then analysed and appropriate distances have been corrected for libration (Cruickshank, 1956) using shape parameters q^2 of 0.08 for all atoms involved. The uncorrected bond lengths along with the corrected values are listed in Table 2 and the bond angles in Table 3.

The molecule assumes the conformation found in other dmg–cobalt(III) complexes (Bigotto, Zangrando

---

† Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38395 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

* Dimethylglyoxime is 2,3-butanedione dioxime.

Table 1. *Final positional (fractional × 10⁵, H × 10⁴) and isotropic thermal parameters (U × 10³ Å²) with estimated standard deviations in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
Co	715 (2)	15622 (2)	21231 (1)	31
O(1)	11934 (16)	995 (11)	10385 (10)	52
O(2)	−11984 (18)	13749 (11)	38176 (9)	53
O(3)	−10011 (18)	30395 (12)	32216 (11)	55
O(4)	14722 (15)	17532 (12)	4704 (10)	50
N(1)	5225 (15)	2995 (11)	17878 (10)	37
N(2)	−6323 (15)	9084 (12)	31256 (9)	37
N(3)	−3306 (17)	28350 (11)	24670 (11)	41
N(4)	8575 (15)	22176 (12)	11412 (10)	39
N(5)	21661 (18)	16562 (13)	27886 (12)	51
N(6)	24370 (17)	15322 (13)	35968 (12)	47
N(7)	28165 (29)	14048 (28)	43749 (18)	110
N(8)	−20007 (14)	14676 (9)	13866 (9)	31
C(1)	3465 (43)	−14119 (18)	21159 (27)	70
C(2)	1241 (19)	−3784 (14)	23146 (13)	43
C(3)	−5384 (20)	−134 (14)	31193 (13)	42
C(4)	−10331 (32)	−6452 (21)	38530 (20)	63
C(5)	122 (41)	45468 (18)	21733 (27)	70
C(6)	1359 (21)	35043 (14)	19600 (15)	47
C(7)	8343 (20)	31359 (15)	11727 (14)	46
C(8)	14728 (35)	37568 (25)	4724 (24)	72
C(9)	−32972 (19)	16074 (13)	17753 (12)	37
C(10)	−47518 (19)	15403 (14)	12784 (14)	42
C(11)	−49084 (21)	13341 (16)	3471 (14)	48
C(12)	−35933 (23)	11836 (20)	−553 (15)	58
C(13)	−21660 (21)	12545 (17)	4807 (13)	46
H1(C1)	443 (54)	−1798 (32)	2599 (30)	137 (15)
H2(C1)	−250 (59)	−1646 (29)	1712 (31)	128 (18)
H3(C1)	1232 (68)	−1372 (40)	1793 (40)	241 (26)
H1(C4)	−229 (36)	−771 (24)	4255 (21)	91 (10)
H2(C4)	−1700 (42)	−318 (26)	4180 (24)	104 (12)
H3(C4)	−1646 (37)	−1151 (26)	3610 (22)	96 (10)
H1(C5)	−631 (56)	4573 (36)	2557 (36)	142 (21)
H2(C5)	725 (48)	4831 (31)	2425 (29)	134 (16)
H3(C5)	−253 (40)	4938 (26)	1643 (24)	106 (12)
H1(C8)	684 (40)	4045 (27)	116 (23)	107 (11)
H2(C8)	2353 (59)	3449 (38)	222 (34)	166 (20)
H3(C8)	1768 (52)	4358 (37)	783 (33)	159 (18)
H(C9)	−3152 (24)	1798 (15)	2436 (15)	47 (5)
H(C10)	−5688 (27)	1600 (16)	1664 (16)	53 (6)
H(C11)	−5903 (28)	1235 (18)	22 (16)	65 (7)
H(C12)	−3673 (25)	994 (17)	−661 (16)	59 (6)
H(C13)	−1208 (23)	1177 (15)	176 (14)	49 (6)
H(1)	1411 (38)	1035 (28)	670 (24)	116 (12)
H(2)	−1078 (39)	2398 (30)	3548 (24)	115 (12)

Table 2. *Bond lengths (Å) with estimated standard deviations in parentheses*

	Uncorrected	Corrected		Uncorrected	Corrected
Co−N(1)	1·8886 (15)	1·898	N(5)−N(6)	1·177 (2)	
Co−N(2)	1·8936 (14)	1·900	N(6)−N(7)	1·146 (3)	
Co−N(3)	1·8956 (16)	1·902	N(8)−C(9)	1·349 (2)	1·354
Co−N(4)	1·9030 (14)	1·910	N(8)−C(13)	1·336 (2)	1·345
Co−N(5)	1·9500 (16)		C(1)−C(2)	1·492 (3)	1·495
Co−N(8)	1·9733 (13)	1·977	C(2)−C(3)	1·467 (3)	1·473
O(1)−N(1)	1·3363 (19)	1·341	C(3)−C(4)	1·494 (3)	1·497
O(2)−N(2)	1·3493 (19)	1·351	C(5)−C(6)	1·498 (3)	1·501
O(3)−N(3)	1·3442 (20)	1·349	C(6)−C(7)	1·463 (3)	1·470
O(4)−N(4)	1·3442 (20)	1·346	C(7)−C(8)	1·503 (3)	1·507
N(1)−C(2)	1·297 (3)	1·301	C(9)−C(10)	1·373 (2)	1·376
N(2)−C(3)	1·292 (3)	1·297	C(10)−C(11)	1·370 (3)	1·380
N(4)−C(7)	1·286 (3)	1·290	C(11)−C(12)	1·377 (3)	1·381
N(3)−C(6)	1·292 (3)	1·297	C(12)−C(13)	1·377 (3)	1·380

Table 3. *Bond angles (°) with estimated standard deviations in parentheses*

| N(1)−Co−N(2)	81·29 (7)	Co−N(4)−C(7)	116·46 (13)
N(1)−Co−N(3)	178·65 (6)	O(4)−N(4)−C(7)	121·24 (16)
N(1)−Co−N(4)	98·45 (7)	Co−N(5)−N(6)	121·80 (14)
N(1)−Co−N(5)	88·59 (7)	N(5)−N(6)−N(7)	174·8 (2)
N(1)−Co−N(8)	90·37 (6)	Co−N(8)−C(9)	121·60 (12)
N(2)−Co−N(4)	177·79 (6)	Co−N(8)−C(13)	120·79 (11)
N(2)−Co−N(3)	99·15 (7)	C(9)−N(8)−C(13)	117·61 (14)
N(2)−Co−N(5)	92·04 (6)	N(1)−C(2)−C(1)	122·8 (2)
N(2)−Co−N(8)	90·66 (6)	N(1)−C(2)−C(3)	112·59 (17)
N(4)−Co−N(3)	81·06 (7)	C(1)−C(2)−C(3)	124·6 (2)
N(4)−Co−N(5)	85·75 (6)	N(2)−C(3)−C(2)	112·68 (16)
N(4)−Co−N(8)	91·54 (6)	N(2)−C(3)−C(4)	124·1 (2)
N(3)−Co−N(5)	90·12 (7)	C(2)−C(3)−C(4)	123·2 (2)
N(3)−Co−N(8)	90·90 (6)	N(3)−C(6)−C(5)	123·4 (2)
N(5)−Co−N(8)	176·93 (6)	N(3)−C(6)−C(7)	112·93 (17)
Co−N(1)−O(1)	122·50 (12)	C(5)−C(6)−C(7)	123·7 (2)
Co−N(1)−C(2)	116·67 (13)	N(4)−C(7)−C(6)	112·96 (16)
O(1)−N(1)−C(2)	120·82 (17)	N(4)−C(7)−C(8)	123·0 (2)
Co−N(2)−O(2)	122·12 (13)	C(6)−C(7)−C(8)	124·1 (2)
Co−N(2)−C(3)	116·66 (13)	N(8)−C(9)−C(10)	122·67 (16)
O(2)−N(2)−C(3)	121·21 (15)	C(9)−C(10)−C(11)	119·27 (16)
Co−N(3)−O(3)	122·20 (13)	C(10)−C(11)−C(12)	118·54 (17)
Co−N(3)−C(6)	116·46 (14)	C(11)−C(12)−C(13)	119·52 (19)
O(3)−N(3)−C(6)	121·27 (18)	N(8)−C(13)−C(12)	122·39 (17)
Co−N(4)−O(4)	122·23 (12)		
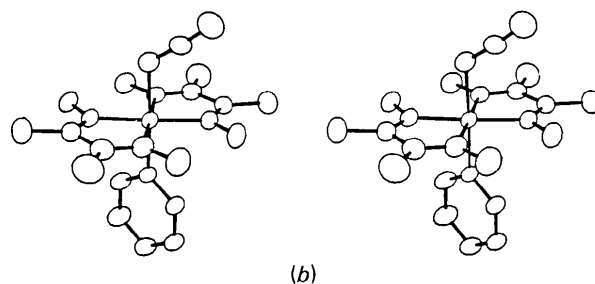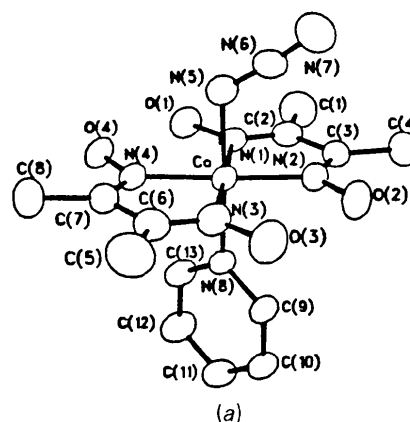
Fig. 1. (a) Projection and (b) stereodiagram of the title compound. Thermal ellipsoids are at 50% probability.

& Randaccio, 1976; Lenhert, 1967; Bresciani-Pahor, Calligaris & Randaccio, 1978), with a roughly planar Co(dmg)₂ arrangement. The two dmg units are linked by two intramolecular O−H···O hydrogen bonds [O(1)···O(4) 2·480 (2), O(2)···O(3) 2·499 (2) Å], and the difference Fourier map indicates that the two H atoms are bonded to O(3) and O(4) of the same ligand, at distances of 1·02 and 1·05 (4) Å, respectively. The arrangement is thus Co(dmg)(H₂dmg), where H₂dmg = dimethylglyoxime, as found in related complexes (Bresciani-Pahor, Calligaris & Randaccio, 1978; Palenik, Sullivan & Naik, 1976; McFadden & McPhail, 1974; Brückner & Randaccio, 1974).

The planes passing through the atoms of the two dmg units make an angle of 3·4 (1)°; their angles with the mean plane of the four nitrogen donor atoms, 3·8 (1) and 0·97 (4)°, are consistent with the values of Brückner & Randaccio (1974). The average bond distances of the dmg ligand, $N-C(sp^2) = 1\cdot292$ (3), $N-O = 1\cdot344$ (2), $C(sp^2)-C(sp^3) = 1\cdot497$ (3), and $C(sp^2)-C(sp^2) = 1\cdot465$ (3) Å (1·296, 1·347, 1·500, and 1·472 Å, respectively after libration correction), are close to the corresponding values found in other transition-metal complexes (Brückner & Randaccio, 1974; Adams & Lenhert, 1973; McFadden & McPhail, 1974; Lenhert, 1967; Battaglia, Corradi, Palmieri, Nardelli & Tani, 1974).

The azide group and the pyridine ring are bonded to the metal atom above and below the equatorial Co(dmg)₂ plane, thus completing octahedral coordination at Co. The average Co—N distance for the equatorial ligands is 1·895 (2) Å (1·903 Å after libration correction), in good agreement with corresponding mean values for similar Co—N bonds of 1·90 Å (Brückner, Calligaris, Nardin & Randaccio, 1970) and 1·89 Å (Crumbliss, Bowman, Gaus & McPhail, 1973). The difference in lengths of the Co—N bonds on the dmg side [1·891 (1) Å] to that of the H₂dmg side [1·899 (1) Å] is significant. Bonds to azide and pyridine are slightly longer at 1·950 (2) and 1·973 (1) Å.

The N(5)—N(6)—N(7) angle of 174·8 (2)° in the azide group is significantly different from 180° but lies within the range of values found for other azides (Allen, Buckland & Nowell, 1976; Mugnoli, Mariani & Simonetta, 1965; Kálmán, Ignáth, Simon, Bognár & Makleit, 1976). The two N—N bond lengths of this group [1·177 (2), 1·146 (3) Å] deviate slightly from those found in earlier studies (Sasvári, Simon, Bognár & Makleit, 1974; Klaska, Jarchow, Günther & Paulsen, 1978).

The pyridine ring is planar [± 0·005 (2) Å] and subtends an angle of 89·5 (2)° with the Co—N plane of the dimethylglyoxime ligands and bisects the angles N(1)—Co—N(4) and N(2)—Co—N(3). This is in agreement with the other structures reported elsewhere (Adams & Lenhert, 1973; Lenhert, 1967). The Co—N(py) bond length, 1·973 (1) Å, is significantly different from the value of 2·04 Å found in bis[dimethylglyoximato(1-)](methoxycarbonylmethyl)-pyridinecobalt (Lenhert, 1967).

The molecular packing is controlled by van der Waals forces.

References

ADAMS, W. W. & LENHERT, P. G. (1973). Acta Cryst. B29, 2412–2425.

ALLEN, D. W., BUCKLAND, D. J. & NOWELL, I. W. (1976). J. Chem. Soc. Perkin Trans. 2, pp. 1610–1612.

BATTAGLIA, L. P., CORRADI, A. B., PALMIERI, C. G., NARDELLI, M. & TANI, M. E. V. (1974). Acta Cryst. B30, 1114–1116.

BIGOTTO, A., ZANGRANDO, E. & RANDACCIO, L. (1976). J. Chem. Soc. Dalton Trans. pp. 96–104.

BRESCIANI-PAHOR, N., CALLIGARIS, M. & RANDACCIO, L. (1978). Inorg. Chim. Acta, 27, 47–52.

BRÜCKNER, S., CALLIGARIS, M., NARDIN, G. & RANDACCIO, L. (1970). Chem. Commun. pp. 152–153.

BRÜCKNER S. & RANDACCIO, L. (1974). J. Chem. Soc. Dalton Trans. pp. 1017–1022.

BUSING, W. R. & LEVY, H. A. (1967). Acta Cryst. 22, 457–464.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORFFE. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). Acta Cryst. 18, 1035–1038.

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

CRUICKSHANK, D. W. J. (1956). Acta Cryst. 9, 747–753.

CRUMBLISS, A. L., BOWMAN, J. T., GAUS, P. L. & McPHAIL, A. T. (1973). Chem. Commun. pp. 415–416.

JOHNSON, C. K. (1976). ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KÁLMÁN, A., IGNÁTH, Z., SIMON, K., BOGNÁR, R. & MAKLEIT, S. (1976). Acta Cryst. B32, 2667–2670.

KLASKA, V. R., JARCHOW, O., GÜNTHER, C. & PAULSEN, H. (1978). Acta Cryst. B34, 226–232.

LENHERT, P. G. (1967). Chem. Commun. pp. 980–982.

McFADDEN, D. L. & McPHAIL, A. T. (1974). J. Chem. Soc. Dalton Trans. pp. 363–366.

MUGNOLI, A., MARIANI, C. & SIMONETTA, M. (1965). Acta Cryst. 19, 367–372.

PALENIK, G. J., SULLIVAN, D. A. & NAIK, D. V. (1976). J. Am. Chem. Soc. 98, 1177–1182.

SASVÁRI, K., SIMON, K., BOGNÁR, R. & MAKLEIT, S. (1974). Acta Cryst. B30, 634–641.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63–76.

SCHRAUZER, G. N. (1968). Acc. Chem. Res. 1, 97–103.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

VIJAYARAGHAVAN, V. R., THILLAICHIDAMBARAM, N., RAGHAVAN, A. & SANTAPPA, M. (1978). J. Indian Chem. Soc. 55, 532–534.