Cd(2) is located on an inversion centre and it is coordinated to four OW molecules and two O(acetato). As in the Co complex the longest Cd—OW length corresponds to that involving the OW with the greatest number of hydrogen bonds.

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Structure of {N,N-Bis[(3,5-dimethylpyrazol-1-yl)methyl]aniline}dinitratocobalt(II)

BY KAJ LOCHER, HENK L. BLONK, WILLEM L. DRIESSEN* AND JAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

Abstract. [Co(NO$_3$)$_2$(C$_{18}$H$_{23}$N$_5$)], $M_r = 492.36$, monoclinic, $P2_1/n$, $a = 8.400$ (2), $b = 14.539$ (2), $c = 17.921$ (3) Å, $\beta = 95.14$ (1)°, $V = 2180$ Å^3, $Z = 4$, $D_x = 1.50$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 8.264$ cm^{-1}, $F(000) = 1020$, $T = 295$ K, final $R = 0.029$ for 1227 significant reflections. The Co^{II} ion is coordinated to three ligand N atoms and to three nitrate O atoms; one nitrate ion coordinates monodentately, and one coordinates bidentately. The geometry of the Co^{II} ion can be described as being intermediate between a distorted trigonal bipyramid and a square pyramid, in which the O atoms of the bidentately coordinating nitrate group are considered to occupy one donor site. Co—N distances are 2.044 (5) and 2.051 (5) Å for the pyrazole N atoms and 2.401 (5) Å for the aniline N atom. Co—O distances are 2.045 (5) Å for the monodentately coordinating nitrate and 2.036 (5) and 2.470 (5) Å for the nitrate which coordinates anisobidentately.

Introduction. Bis[(3,5-dimethylpyrazol-1-yl)methyl]aniline (abbreviated pabd) forms a variety of complexes with transition-metal ions. The synthesis and characterization of these compounds and the X-ray structures of [CoCl$_2$(pabd)] and [CuBr$_2$(pabd)] have been described (Blonk, Driessen & Reedijk, 1985).

* To whom correspondence should be addressed.

From ligand-field data a distorted five-coordinate structure was proposed for the title compound, [Co(NO$_3$)$_2$(pabd)]. From infrared data it was proposed that one nitrate group might be coordinated monodentately and one might be coordinated bidentately, and that the aniline N atom would hardly take part in the coordination, if at all (Blonk *et al.*, 1985).

Experimental. Red crystals grown from acetonitrile at room temperature. Crystal approximately 0.5 × 0.2 × 0.2 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$. Cell constants from setting angles of 24 reflections, $10.1 \leq \theta \leq 11.6°$. Corrections for Lorentz and polarization effects. No absorption correction applied (transmission coefficients 0.92 to 1.04). $\theta_{max} = 22.0°$; h 0 to 8, k 0 to 15, l −18 to 18. Standard reflections $1\overline{1}9$, $3\overline{5}1$ and $0\overline{5}\overline{8}$, intensity variation 10.64%, corrections applied accordingly. 3027 measured reflections, 2797 independent, $R_{int} = 0.052$, 1570 unobserved with $I < 2\sigma(I)$. Structure solved by Patterson method, F used in LS refinement. Two thirds of the H atoms found in difference Fourier maps; the others placed at 0.95 Å from the parent atoms. Least-squares refinement of positional and anisotropic thermal parameters of non-H atoms; positional parameters of H atoms coupled to parent atoms; fixed isotropic thermal factor of 5.2 Å^2 for the H atoms. $S = 0.828$, $w = 1/\sigma^2(F)$, $R = 0.029$,

$[Co(NO_3)_2(C_{18}H_{23}N_5)]$

Table 1. *Fractional coordinates* (Co: $\times 10^5$; *others*: $\times 10^4$) *and equivalent isotropic thermal parameters* (Co: $\times 10^2$ Å^2; *others*: $\times 10$ Å^2)

$B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{U}$. E.s.d.'s in the least-significant digits are given in parentheses.

	x	y	z	B_{eq}
Co	87462 (10)	25037 (7)	53070 (4)	287 (2)
N(10)	11094 (6)	3236 (3)	4914 (3)	26 (2)
C(11)	10944 (8)	3682 (5)	4179 (4)	27 (2)
C(12)	11745 (9)	4461 (5)	4038 (4)	37 (2)
C(13)	11535 (11)	4873 (5)	3347 (5)	51 (3)
C(14)	10539 (11)	4498 (6)	2785 (4)	52 (3)
C(15)	9770 (10)	3693 (6)	2912 (4)	51 (3)
C(16)	9952 (9)	3277 (5)	3610 (4)	39 (2)
C(20)	12224 (7)	2460 (6)	4937 (3)	29 (2)
N(21)	11410 (6)	1670 (3)	4584 (3)	26 (2)
N(22)	9838 (6)	1519 (3)	4718 (3)	26 (2)
C(23)	9411 (7)	764 (4)	4304 (3)	29 (2)
C(24)	10696 (9)	457 (5)	3940 (4)	35 (2)
C(25)	11935 (8)	1047 (5)	4124 (3)	30 (2)
C(26)	7768 (10)	397 (6)	4263 (4)	41 (2)
C(27)	13590 (11)	1014 (7)	3924 (5)	58 (3)
C(30)	11530 (9)	3885 (5)	5531 (4)	33 (2)
N(31)	11323 (6)	3434 (4)	6232 (3)	31 (2)
N(32)	10062 (6)	2851 (3)	6286 (3)	31 (2)
C(33)	10135 (8)	2613 (5)	7012 (3)	38 (2)
C(34)	11415 (10)	3043 (5)	7398 (4)	45 (2)
C(35)	12142 (8)	3575 (5)	6903 (4)	36 (2)
C(36)	8982 (13)	1975 (7)	7310 (5)	61 (4)
C(37)	13578 (12)	4162 (7)	7005 (5)	56 (3)
N(40)	6608 (8)	3493 (5)	4479 (3)	46 (2)
O(41)	7749 (5)	3722 (3)	4954 (2)	39 (1)
O(42)	5699 (7)	4059 (4)	4200 (4)	90 (2)
O(43)	6528 (6)	2655 (4)	4312 (3)	53 (2)
N(50)	5857 (8)	1913 (5)	5916 (3)	40 (2)
O(51)	7151 (6)	1596 (3)	5693 (2)	41 (2)
O(52)	5746 (7)	2747 (4)	6002 (3)	63 (2)
O(53)	4794 (6)	1379 (4)	6031 (3)	57 (2)

$wR = 0.036$. $\Delta_{max}/\sigma < 0.20$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0.23, −0.20 e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (Amdahl V7B); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond distances and selected angles are in Table 2. An *ORTEP* drawing (Johnson, 1965) of [Co(NO$_3$)$_2$(pabd)] and the atomic labelling are given in Fig. 1.

Taking the plane formed by the atoms N(22) and N(32) and the mean position of O(41) and O(43) as base, then the structural index τ (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984) is 0.58. This value is intermediate between square pyramidal ($\tau = 0.0$) and trigonal bipyramidal ($\tau = 1.0$). The two coordinating bidentate nitrate O atoms form a bite angle of only 55.7 (2)° with the Co ion. Several authors have

proposed that such a bidentate anion could be considered as occupying one coordination site of the metal complex (Cotton, Goodgame & Sonderberg, 1963; Garner & Wallwork, 1966). These pseudo five-coordinate stereochemistries correlated well with the observed spectral and magnetic properties (Goodgame, Goodgame & Rayner Canham, 1969). Such a pseudo monodentate nitrate coordination, or anisobidentate coordination (Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985), can

Table 2. *Intramolecular distances* (Å) *and selected angles* (°)

Co–N(10)	2.401 (5)	C(23)–C(24)	1.385 (9)
Co–N(22)	2.044 (5)	C(23)–C(26)	1.476 (10)
Co–N(32)	2.051 (5)	C(24)–C(25)	1.365 (9)
Co–O(41)	2.036 (5)	C(25)–C(27)	1.467 (11)
Co–O(43)	2.470 (5)	C(30)–N(31)	1.441 (8)
Co–O(51)	2.045 (5)	N(31)–N(32)	1.367 (7)
N(10)–C(11)	1.464 (7)	N(31)–C(35)	1.347 (7)
N(10)–C(20)	1.472 (9)	N(32)–C(33)	1.343 (7)
N(10)–C(30)	1.475 (8)	C(33)–C(34)	1.376 (9)
C(11)–C(12)	1.352 (9)	C(33)–C(36)	1.475 (12)
C(11)–C(16)	1.388 (9)	C(34) C(35)	1.362 (10)
C(12)–C(13)	1.372 (10)	C(35)–C(37)	1.476 (12)
C(13)–C(14)	1.363 (11)	N(40)–O(41)	1.269 (7)
C(14)–C(15)	1.366 (11)	N(40)–O(42)	1.200 (7)
C(15)–C(16)	1.386 (10)	N(40)–O(43)	1.255 (7)
C(20)–N(21)	1.453 (9)	N(50)–O(51)	1.277 (7)
N(21)–N(22)	1.381 (7)	N(50)–O(52)	1.227 (7)
N(21)–C(25)	1.328 (7)	N(50)–O(53)	1.215 (7)
N(22)–C(23)	1.354 (7)		

N(22)–Co–N(32)	112.5 (2)	N(10)–Co–O(41)	81.3 (2)
N(22)–Co–O(51)	93.5 (2)	N(22)–Co–O(43)	91.9 (2)
N(10)–Co–N(32)	75.4 (2)	N(32)–Co–O(41)	103.1 (2)
N(10)–Co–O(43)	109.6 (2)	N(32)–Co–O(43)	155.4 (2)
O(43)–Co–O(51)	80.0 (2)	O(41)–Co–O(43)	55.7 (2)
N(22)–Co–O(41)	129.8 (2)	O(41)–Co–O(51)	113.8 (2)
N(32)–Co–O(51)	100.9 (2)	Co–N(10)–C(30)	102.7 (4)
N(10)–Co–O(51)	164.9 (2)	Co–N(10)–C(11)	117.0 (4)
N(10)–Co–N(22)	75.0 (2)	Co–N(10)–C(20)	101.4 (4)

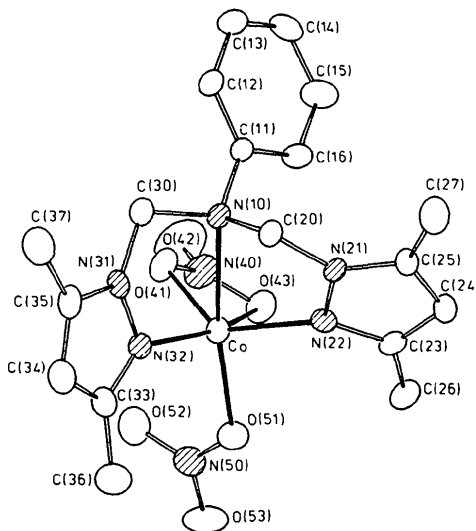|	
C(20)–N(10)–C(30)	110.7 (5)
C(11)–N(10)–C(30)	112.7 (5)
C(11)–N(10)–C(20)	111.6 (5)

Fig. 1. *ORTEP* drawing and atomic labelling of [Co(NO$_3$)$_2$(pabd)].

also be considered to be present in the title compound, which is in good agreement with the observed ligand-field spectrum (solid-state reflectance electronic spectrum in the visible and near infrared) of this compound (Blonk *et al.*, 1985).

Spectroscopic data could not predict that the aniline N would take part in the coordination (Blonk *et al.*, 1985). However, the aniline N is clearly coordinated to the Co ion. Thus the angles around the aniline N do not diverge greatly from ideal tetrahedral values (see Table 2). In |CuBr$_2$(pabd)| the aniline N is also coordinated (Blonk *et al.*, 1985). On the other hand, in [CoCl$_2$(pabd)] the aniline N is not coordinated to the Co ion (Blonk *et al.*, 1985). In similar complexes, with a nitroxyl spin label in place of the aniline, the metal–nitroxyl electron-electron exchange interaction has been found to be dependent on solvent, temperature and the presence or absence of methyl substituents on the pyrazole rings. These data suggest that the strength of the metal bond to the central N of the ligand may vary substantially from one complex to another (Eaton & Eaton, 1986). The phenyl ring and the pyrazole rings are planar (distances to the least-squares planes less than 0·015 Å) and the methyl C atoms are coplanar with the respective pyrazole rings (distances to the least-squares planes less than 0·08 Å). The pyrazole rings are neither coplanar with the phenyl ring [interplanar angles 74·8 (3) and 161·3 (3)°] nor mutually coplanar [116·5 (3)°].

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Reactions of Coordinated Molecules. 44. Structure of a Diels–Alder Adduct of an Organometallic Dienophile

BY P. GALEN LENHERT,* C. M. LUKEHART* AND LOUANN SACKSTEDER

Departments of Chemistry and Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

Abstract. Difluoro[1-(1,2,4-trimethylcyclohex-3-en-1-yl)-2-(carbonylcyclopentadienylferra)butene-1,3-dionato-O,O']boron, (η-C$_5$H$_5$)(OC)Fe(MeC$\overline{O}$)-{[CH$_2$CH$_2$(Me)C=CHCH(Me)C(Me)]C$\underline{O}$}BF$_2$, $M_r = 392·04$, monoclinic, $P2_1/c$, $a = 7·161$ (1), $b = 16·850$ (3), $c = 16·230$ (3) Å, $\beta = 111·77$ (2)°, $V = 1818·72$ Å^3, $Z = 4$, $D_x = 1·432$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8·59$ cm^{-1}, $F(000) = 816$, $T = 294$ K. Final $R = 0·050$ for 4172 observed reflections. The structure of the substituted cyclohexene formed by cycloaddition of *trans*-2-methyl-1,3-pentadiene to a methacryl (ferra-β-diketonato)BF$_2$ complex confirms the regiochemistry and the stereochemistry of the Diels–Alder reaction. The '*ortho, para*' regioisomer is formed, and the highly stereoselective formation of one diastereomer is established. The ferra-β-diketonato substituent adopts a boat-shaped conformation having the cyclopentadienyl ligand in an axial position.

Introduction. When the complex (η-C$_5$H$_5$)(OC)Fe-(MeC$\overline{O}$)[(methacryl)C$\underline{O}$]BF$_2$ (Lenhert, Lukehart & Sacksteder, 1986*b*) is treated with isoprene, 2,3-dimethyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene and cyclopentadiene, it reacts as an activated dienophile to give Diels–Alder cycloaddition products. These adducts are formed with high regio- and stereo-selectivity (Lenhert, Lukehart & Sacksteder, 1986*a*). It is apparent from 400 MHz ^{1}H NMR data of the

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* To whom correspondence should be addressed.