The coordination about Ni is distorted octahedral, with bonds being formed to the oxime, imine and amine N atoms of the hexadentate ligand. The average Ni—N(amine) and Ni—N(imine) distances (2·127 and 2·019 Å, respectively) are normal and agree well with the corresponding bond lengths in comparable Ni^{II} complexes.

In an earlier paper we concluded that in octahedral Ni^{II} complexes deprotonation of the coordinated oxime group is accompanied by a shortening of about 0·1 Å in the Ni—N(oxime) bond length, from *ca* 2·10 to 2·01 Å (Korvenranta, Saarinen & Näsäkkälä, 1982). The Ni—N(oxime) distance found here (2·126 Å) is consistent with the bond length in typical undissociated structures.

The N—O and C—N(oxime) bond lengths and the C—N—O bond angle in the complex are 1·357 (5), 1·286 (6) Å, and 115·7 (4)°, respectively. Even though the C—N—O angle is relatively large, all these values are in satisfactory agreement with the ranges 1·38 ±0·03, 1·29±0·02 Å, and 112±2° reported for the undissociated oxime group and deviate considerably from the corresponding range 1·26±0·01, 1·36 ±0·02 Å, and 121±2° found for several octahedral oximato structures (Korvenranta, Saarinen & Näsäkkälä, 1982). In sum, an H atom symmetrically disposed in the O···O bond between two oximato O atoms seems to be sufficient to fix the geometry of the NOH function, and in its essential features the present complex generally resembles those of other octahedral Ni^{II} complexes formed without loss of the oxime proton.

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The Structure of the Mixed-Ligand Compound {*N,N*-Bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline}(3,5-dimethylpyrazole)nitratozinc(II) Nitrate

BY WILLEM L. DRIESSEN,* HENK L. BLONK, RUDOLF A. G. DE GRAAFF AND JAN REEDIJK

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

(*Received* 9 *February* 1987; *accepted* 25 *March* 1987)

Abstract. $[Zn(C_5H_8N_2)(C_{18}H_{23}N_5)(NO_3)]NO_3$, M_r = 594·93, triclinic, $P\bar{1}$, a = 12·932 (3), b = 15·402 (15), c = 15·451 (2) Å, α = 90·91 (4), β = 108·61 (2), γ = 107·03 (4)°, V = 2768·3 Å^3, Z = 4, D_x = 1·43 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, μ = 9·58 cm^{-1}, $F(000)$ = 1241, T = 293 K, final R = 0·037 for 3154 significant reflections. The asymmetric unit consists of two different formula units of almost identical dimensions. In each of these molecules Zn is tetrahedrally surrounded by two azole N atoms of the ligand *N,N*-bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline (pabd), by an azole N atom of 3,5-dimethylpyrazole and an O atom of one of the nitrate anions. Distances from Zn to the donor atoms are in the narrow range of 1·98 to 2·06 Å. The 3,5-dimethylpyrazole ligand is hydrogen bonded, through the H atom on the other azole N atom, to the second nitrate ion, with an N···O distance of 2·72 Å. The aniline N atom of pabd does not participate in the coordination. Bond angles around this N atom are close to 120°, indicating a delocalized lone pair of electrons.

Introduction. The synthesis and characterization of several transition-metal compounds of *N,N*-bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline (pabd) have been described recently (Blonk, Driessen & Reedijk, 1985). Mostly well defined coordination compounds are formed. With some metal salts, however, products have been isolated which contain fragments of pabd. Cluster

* To whom correspondence should be addressed.

0108-2701/87/081516-03$01.50

compounds form with nickel halides in which deprotonated *N*-hydroxymethyl-3,5-dimethylpyrazole, a decomposition product of pabd, is present as the ligand (Paap, Bouwman, Driessen & Reedijk, 1985). With zinc nitrate a coordination compound forms which contains not only the intact ligand pabd but also 3,5-dimethylpyrazole (dmpz). The presence of coordinated dmpz can only be the result of the decomposition of some of the ligand pabd. To gain insight into the stereochemistry of this type of mixed-ligand coordination compound, the crystal structure of the compound Zn(pabd)(dmpz)$(NO_3)_2$ has been solved.

Experimental. White needles grown from ethanol at room temperature with approximate dimensions 0·40 × 0·15 × 0·15 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Cell constants from setting angles of 24 reflections, $10 \le \theta \le 12°$. Corrections for Lorentz and polarization effects. No absorption correction applied (transmission coefficients 0·965 to 1·025). $\theta_{max} = 20°$, h −12 to 12, k −14 to 14, l 0 to 14. Standard reflections 722, $\bar{6}\bar{2}2$ and $\bar{5}08$, intensity variation 3·3%. 5397 measured reflections, 5138 independent, $R_{int} = 0{\cdot}022$, 1984 with $I < 2\sigma(I)$. Heavy atoms located from a Patterson map. Structure solved with the computer program *AUTOFOUR* (Kinneging & de Graaff, 1984). F used in LS refinement. Some of the H atoms found in difference Fourier maps, the others placed at 0·95 Å from the parent atoms. Least-squares refinement of non-H-atom positional and anisotropic thermal parameters; positional parameters of H atoms coupled to parent atoms; fixed isotropic thermal factor of 3·50 Å^2 for the H atoms. $S = 2{\cdot}28$, $w = 1/\sigma^2(F)$, $R = 0{\cdot}037$, $wR = 0{\cdot}047$. $\Delta_{max}/\sigma < 0{\cdot}20$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0·42, −0·46 e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (IBM 3083); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond distances and selected valence angles are given in Table 2. The asymmetric unit consists of two different molecules with almost identical dimensions; therefore, only one of these molecules will be described in detail. An *ORTEP* projection (Johnson, 1965) of one of the molecular entities Zn(pabd)(dmpz)$(NO_3)_2$ and the atomic labelling are given in Fig. 1.

* Lists of H-atom coordinates, anisotropic thermal parameters, valence angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43911 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^2 *for* Zn, Å^2 × 10 *for* C, N, O) *of the non*-H *atoms*

$B_{eq} = (8/3)\,\pi^2$ trace $\tilde{U}$.

	x	y	z	B_{eq}
Zn0	3366 (1)	4252 (1)	7248 (1)	357 (3)
Zn1	6658 (1)	108 (1)	7818 (1)	372 (3)
N2	3305 (5)	2538 (3)	7993 (4)	43 (2)
O3	3280 (4)	3340 (3)	8180 (3)	48 (2)
O4	3059 (4)	1942 (3)	8460 (3)	61 (2)
O5	3533 (6)	2393 (3)	7316 (4)	95 (3)
N6	6669 (5)	−1599 (4)	7014 (4)	54 (2)
O7	6755 (4)	−806 (3)	6882 (3)	60 (2)
O8	6900 (4)	−2122 (3)	6552 (3)	63 (2)
O9	6310 (7)	−1900 (4)	7618 (5)	121 (4)
N10	6611 (4)	5350 (3)	7914 (4)	35 (2)
C11	7811 (5)	5721 (4)	8167 (4)	32 (2)
C12	8516 (5)	5239 (4)	8675 (5)	44 (3)
C13	9695 (6)	5603 (5)	8919 (6)	71 (4)
C14	10184 (6)	6393 (5)	8692 (7)	88 (4)
C15	9527 (6)	6900 (5)	8199 (6)	78 (4)
C16	8343 (5)	6534 (4)	7914 (5)	47 (3)
C20	6027 (5)	4391 (4)	7780 (4)	32 (2)
N21	5354 (4)	4040 (3)	6834 (3)	28 (2)
N22	4240 (4)	4059 (3)	6457 (3)	27 (2)
C23	3934 (5)	3820 (4)	5557 (4)	31 (2)
C24	4833 (5)	3661 (4)	5351 (5)	38 (3)
C25	5720 (5)	3802 (4)	6157 (5)	33 (2)
C26	2777 (5)	3759 (4)	4919 (5)	50 (3)
C27	6884 (5)	3733 (4)	6368 (5)	53 (3)
C30	5881 (5)	5938 (4)	7684 (4)	30 (2)
N31	5286 (4)	5954 (3)	8335 (3)	30 (2)
N32	4210 (4)	5342 (3)	8218 (4)	31 (2)
C33	3948 (5)	5553 (4)	8941 (5)	35 (2)
C34	4849 (5)	6274 (4)	9530 (5)	41 (3)
C35	5675 (5)	6492 (4)	9138 (5)	36 (2)
C36	2850 (5)	5066 (4)	9070 (5)	51 (3)
C37	6820 (5)	7221 (5)	9470 (5)	61 (3)
N41	1338 (4)	4849 (3)	6586 (4)	44 (2)
N42	1689 (4)	4081 (3)	6692 (4)	37 (2)
C43	738 (5)	3393 (4)	6432 (5)	47 (3)
C44	−199 (6)	3692 (5)	6158 (6)	66 (3)
C45	206 (6)	4618 (5)	6274 (6)	57 (3)
C46	766 (6)	2430 (4)	6455 (6)	64 (3)
C47	−367 (7)	5338 (6)	6099 (7)	94 (5)
N50	3412 (4)	−454 (3)	7094 (4)	35 (2)
C51	2194 (5)	−725 (4)	6808 (4)	33 (2)
C52	1641 (5)	−124 (4)	6986 (5)	47 (3)
C53	469 (6)	−383 (5)	6698 (6)	75 (4)
C54	−184 (6)	−1246 (5)	6251 (7)	77 (4)
C55	360 (6)	−1818 (5)	6077 (6)	66 (3)
C56	1531 (5)	−1562 (4)	6330 (5)	46 (3)
C60	4116 (5)	484 (4)	7284 (4)	33 (2)
N61	4724 (4)	758 (3)	6636 (3)	33 (2)
N62	5826 (4)	735 (3)	6808 (3)	33 (2)
C63	6109 (5)	1045 (4)	6090 (4)	34 (2)
C64	5214 (5)	1253 (4)	5461 (5)	42 (3)
C65	4346 (5)	1075 (4)	5817 (5)	39 (3)
C66	7255 (6)	1126 (4)	6021 (5)	54 (3)
C67	3188 (6)	1163 (5)	5447 (5)	58 (3)
C70	4018 (5)	−1129 (4)	7265 (4)	30 (2)
N71	4666 (4)	−1075 (3)	8235 (3)	28 (2)
N72	5782 (4)	−494 (3)	8612 (3)	29 (2)
C73	6089 (5)	−549 (4)	9516 (4)	33 (2)
C74	5190 (5)	−1148 (4)	9724 (5)	36 (2)
C75	4309 (5)	−1450 (4)	8906 (5)	33 (2)
C76	7250 (5)	−40 (4)	10148 (4)	47 (3)
C77	3131 (5)	−2118 (4)	8713 (5)	51 (3)
N81	8695 (4)	1695 (3)	8457 (4)	42 (2)
N82	8330 (4)	776 (3)	8384 (4)	38 (2)
C83	9278 (5)	519 (5)	8596 (5)	45 (3)
C84	10219 (5)	1298 (4)	8781 (6)	59 (3)
C85	9828 (5)	2039 (5)	8703 (5)	48 (3)
C86	9262 (6)	−419 (5)	8613 (5)	69 (4)
C87	10417 (6)	3029 (5)	8825 (6)	88 (4)
N90	6763 (5)	3475 (3)	3835 (4)	48 (2)
O91	6611 (4)	4211 (3)	3963 (4)	57 (2)
O92	7321 (4)	3403 (3)	3330 (4)	62 (2)
O93	6397 (7)	2798 (3)	4186 (5)	118 (4)
N95	6717 (5)	2419 (4)	8811 (4)	50 (2)
O96	6577 (4)	1588 (3)	8913 (3)	52 (2)
O97	7365 (4)	2813 (3)	8407 (4)	67 (2)
O98	6197 (7)	2819 (5)	9084 (5)	128 (4)

The Zn^{II} ion is tetrahedrally surrounded by two azole N atoms of the ligand pabd, by an azole N atom of dmpz and an O atom of one of the nitrate anions. Distances from Zn to the donor atoms lie in the narrow range of 1·98 to 2·06 Å. The coordination geometry about Zn deviates from an ideal tetrahedron, the angles vary from 93·8 (2)° for O3—Zn0—N32 to 119·9 (2)° for N22—Zn0—N42.

Table 2. *Bond lengths* (Å) *and selected valence angles* (°) *for* $Zn(pabd)(dmpz)(NO_3)_2$

Zn0—O3	2·033 (5)	C43—C44	1·366 (9)
Zn0—N22	1·981 (5)	C43—C46	1·495 (9)
Zn0—N32	2·016 (5)	C44—C45	1·35 (1)
Zn0—N42	1·995 (5)	C45—C47	1·488 (9)
Zn1—O7	2·061 (5)	N50—C51	1·419 (7)
Zn1—N62	2·026 (5)	N50—C60	1·430 (7)
Zn1—N72	1·989 (5)	N50—C70	1·456 (7)
Zn1—N82	1·990 (5)	C51—C52	1·396 (8)
N2—O3	1·275 (6)	C51—C56	1·364 (9)
N2—O4	1·208 (7)	C52—C53	1·365 (9)
N2—O5	1·208 (8)	C53—C54	1·38 (1)
N6—O7	1·220 (7)	C54—C55	1·35 (1)
N6—O8	1·226 (7)	C55—C56	1·366 (9)
N6—O9	1·211 (9)	C60—N61	1·456 (8)
N10—C11	1·405 (7)	N61—N62	1·375 (6)
N10—C20	1·426 (7)	N61—C65	1·358 (8)
N10—C30	1·461 (7)	N62—C63	1·330 (8)
C11—C12	1·400 (8)	C63—C64	1·376 (9)
C11—C16	1·370 (9)	C63—C66	1·489 (9)
C12—C13	1·381 (9)	C64—C65	1·362 (9)
C13—C14	1·31 (1)	C65—C67	1·471 (9)
C14—C15	1·38 (1)	C70—N71	1·452 (8)
C15—C16	1·382 (9)	N71—N72	1·383 (6)
C20—N21	1·440 (8)	N71—C75	1·338 (8)
N21—N22	1·380 (6)	N72—C73	1·337 (8)
N21—C25	1·363 (8)	C73—C74	1·388 (9)
N22—C23	1·332 (8)	C73—C76	1·474 (8)
C23—C24	1·383 (8)	C74—C75	1·365 (9)
C23—C26	1·482 (8)	C75—C77	1·500 (8)
C24—C25	1·360 (9)	N81—N82	1·345 (7)
C25—C27	1·472 (8)	N81—C85	1·325 (8)
C30—N31	1·452 (8)	N82—C83	1·341 (8)
N31—N32	1·387 (6)	C83—C84	1·382 (9)
N31—C35	1·342 (8)	C83—C86	1·440 (9)
N32—C33	1·328 (8)	C84—C95	1·37 (1)
C33—C34	1·397 (9)	C85—C87	1·470 (9)
C33—C36	1·476 (9)	N90—O91	1·230 (7)
C34—C35	1·353 (9)	N90—O92	1·244 (7)
C35—C37	1·497 (8)	N90—O93	1·223 (7)
N41—N42	1·380 (6)	N95—O96	1·258 (7)
N41—C45	1·320 (8)	N95—O97	1·228 (7)
N42—C43	1·306 (8)	N95—O98	1·194 (7)

O3—Zn0—N22	113·3 (2)	O7—Zn1—N62	92·2 (2)
O3—Zn0—N32	93·8 (2)	O7—Zn1—N72	113·1 (2)
O3—Zn0—N42	98·2 (2)	O7—Zn1—N82	98·1 (2)
N22—Zn0—N32	114·1 (2)	N62—Zn1—N72	115·7 (2)
N22—Zn0—N42	119·9 (2)	N62—Zn1—N82	113·3 (2)
N32—Zn0—N42	113·1 (2)	N72—Zn1—N82	119·4 (2)

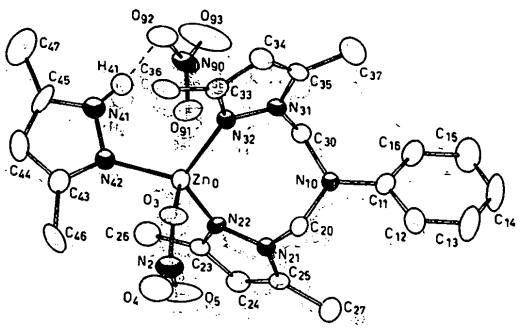

Fig. 1. *ORTEP* projection (Johnson, 1965) and atomic labelling of the molecular entity $Zn(pabd)(dmpz)(NO_3)_2$. For clarity the H atoms are omitted, except those that take part in hydrogen bonding.

The dmpz molecule is not only coordinated to the Zn atom but is also hydrogen bonded, through the H atom on the other azole N atom, to the second nitrate, with an N41···O92 distance of 2·72 Å. The occurrence of the N—H-stretching vibration band at 3180 cm^{-1} indicates a very strong hydrogen bond to the nitrate ion (Bellamy & Owen, 1969; Reedijk, Windhorst, van Ham & Groeneveld, 1971).

The precise coordination mode of the nitrates could not be inferred from the infrared spectrum as strong ligand bands occur in the same region as the nitrate absorptions; however, from the occurrence of a band at 1740 cm^{-1} with shoulders at 1716 and 1760 cm^{-1} (nitrate combination bands) it was clear that at least one of the nitrate ions was coordinated (Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985).

There is no bond between the aniline N atom of the pabd ligand and the Zn^{II} ion as the Zn0···N10 distance is 3·82 Å. The bond angles around the aniline N atom are close to 120°, which indicates that the lone pair of electrons on this N atom conjugates with the π electrons of the phenyl ring. The presence of an absorption band of medium intensity at 938 cm^{-1} is in accordance with this non-coordination of the aniline N atom (Blonk *et al.*, 1985).

The nitrate ions, the phenyl ring and the pyrazole rings are planar (distances to the least-squares planes do not exceed 0·04 Å). The pyrazole rings are neither coplanar with the phenyl ring nor mutually coplanar. There is no intermolecular stacking of the aromatic rings. The packing of the molecules is due to normal van der Waals contacts.

The authors are indebted to S. Gorter for his assistance in the collection and processing of the diffraction data.

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