

The Cu—O bond lengths are of the same order of magnitude as those found in other similar copper complexes (Carmichael, Steinrauf & Belford, 1965; Hon, Pfluger & Belford, 1966). The C—O bonds have been reported to show some important differences depending on whether the group bonded to the C atom is capable of conjugation with the chelate ring. Nevertheless, the values observed in this case are similar to those described in cases where alkyl groups are bonded to the C atom and both values are essentially the same.

The remaining bonds of the chelate ring, C(1)—C(2) and C(2)—C(7), have bond lengths of 1.392 (7) and 1.401 (7) Å, significantly shorter than the other C—C distances in the complex (av. 1.513 Å) suggesting an increase in the order of the bond. This must be caused by an electronic delocalization within the chelate ring. The unsaturated character of the C(1)—C(2) bond is further supported by the half-chair conformation of the cyclohexane ring, similar to that observed in cyclohexene (Eliei, Allinger, Angyol & Morrison, 1967).

There are no short intermolecular interactions between the C(3) and Cu atoms like those described for copper acetylacetonate [Dahl; unpublished results referred to by Robertson & Truter (1967)], copper ethylacetylacetonate (Hall, McKinnon & Waters, 1966) and copper 1-phenyl-1,3-butanedionate (Hon, Pfluger & Belford, 1966). It has been proposed that the

presence of an H atom on the γ -C atom is necessary for such an interaction to take place (Robertson & Truter, 1967).

The complex reported herein is almost completely planar, with the atoms forming the chelate ring and C(3) and C(6) showing a maximum deviation of 0.10 Å from the plane while atoms C(4) and C(5) deviate about equally in opposite directions from the plane.

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Structure of Bis[*N,N*-bis(1-pyrazolylmethyl)amine]nickel(II) Bis(tetrafluoroborate)

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Abstract. $[\text{Ni}(\text{C}_8\text{H}_{11}\text{N}_3)_2](\text{BF}_4)_2$, $M_r = 586.71$, orthorhombic, $P2_12_12_1$, $a = 10.255$ (1), $b = 13.734$ (2), $c = 17.995$ (1) Å, $V = 2534.5$ (5) Å³, $Z = 4$, $D_x = 1.538$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 18.8$ cm⁻¹, $F(000) = 1192$, $T = 295$ K, $R = 0.076$ for 1845 observed reflections with $I > 2.5\sigma(I)$. The BF_4 anions show some disorder. The Ni^{II} ion is surrounded by four azole nitrogens at 2.02 (1) to 2.07 (1) Å and two amine

nitrogens at 2.17 (1) and 2.182 (9) Å in an almost octahedral geometry. The two ligands are in a *fac* arrangement. The cation has non-crystallographic twofold axial symmetry. The ligands are weakly hydrogen bonded through the H atoms on the amine nitrogens to the fluoroborate anions with N...F distances of 2.82 (1) and 2.97 (1) Å.

Introduction. Several transition-metal compounds of tris(3,5-dimethyl-1-pyrazolylmethyl)amine have been

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described recently (van Driel, Driessen & Reedijk, 1985). Well defined coordination compounds are obtained with this ligand. With the analogous ligand tris(1-pyrazolylmethyl)amine not only do coordination compounds form in which the ligand is intact (Ochocki, Driessen, de Graaff & Reedijk, 1988), but also coordination compounds in which the ligand has lost one of its pyrazole groups, e.g. bis(1-pyrazolylmethyl)amine (am2p) (Driessen, de Graaff & Wiesmeijer, 1987). With other pyrazole-substituted amines coordination compounds have also been isolated which contain fragments of the original ligands (Paap, Bouwman, Driessen & Reedijk, 1985; Driessen, Blonk, de Graaff & Reedijk, 1987). In am2p, the secondary amine nitrogen now bears a hydrogen available for hydrogen-bond formation. This may give additional stability to the am2p compounds. To gain insight into the stereochemistry of this type of coordination compound, the crystal structure of the compound [Ni(am2p)₂](BF₄)₂ has been determined.

Experimental. Transparent violet crystals were grown from ethanol at room temperature. A suitable crystal (0.30 × 0.42 × 0.42 mm) was mounted inside a Lindemann-glass capillary. Data were collected (de Boer & Duisenberg, 1984) with an Enraf-Nonius CAD-4F diffractometer using Ni-filtered Cu K α radiation. Unit-cell parameters and their e.s.d.'s were derived from the setting angles of 20 reflections with 20 < 2 θ < 30°. Intensity data for 2745 reflections [h 0:12, k 0:16, l 0:21; 2.46 < θ < 70°] were collected in the $\omega/2\theta$ scan mode with $\Delta\omega = 0.50 + 0.15 \tan\theta^\circ$. Two reference reflections (200, 011) measured every hour of X-ray exposure indicated a small linear decay of 5% over 53.5 h of X-ray exposure time. The intensity data were corrected for this decay, for Lp and for absorption (after isotropic refinement; correction range 0.777 to 1.344) with the program *DIFABS* (Walker & Stuart, 1983). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.003I)^2$ following McCandlish, Stout & Andrews (1975), resulting in 1845 reflections with $I > 2.5\sigma(I)$ and $\sum\sigma/\sum I = 0.012$. The space group was derived from the observed systematic absences. The structure was solved with Patterson and Fourier methods (*SHELXS86*; Sheldrick, 1986) and refined on F with *SHELX76* (Sheldrick, 1976). Both anions show high anisotropic thermal parameters and one anion significant disorder (0.81:0.19). H atoms were introduced on calculated positions (C—H = 0.98 Å) and refined with fixed geometry with respect to their carrier atoms. Refinement with weights based on $w = 1/\sigma^2(F)$ and B—F and F—F distance restraints converged at $R = 0.076$ [$wR = 0.052$; $S = 1.54$; 354 parameters; $(\Delta/\sigma)_{\max} = 0.5$]. The relatively high R value is probably related

Table 1. Final coordinates and equivalent isotropic thermal parameters and their e.s.d.'s in parentheses

Starred atoms are disordered [population 0.81 (1)].

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq} (Å ²)
Ni	0.3879 (2)	0.4474 (1)	0.15432 (9)	0.0637 (6)
N(1)	0.479 (1)	0.5207 (6)	0.0601 (5)	0.067 (4)
N(2)	0.215 (1)	0.3899 (6)	0.1003 (5)	0.072 (4)
N(11)	0.347 (1)	0.6462 (8)	0.1121 (6)	0.081 (4)
N(12)	0.3116 (8)	0.5838 (5)	0.1643 (6)	0.070 (3)
N(21)	0.644 (1)	0.5261 (6)	0.1526 (6)	0.081 (4)
N(22)	0.5622 (9)	0.4834 (6)	0.1992 (6)	0.067 (4)
N(31)	0.364 (1)	0.2574 (8)	0.0899 (5)	0.075 (4)
N(32)	0.453 (1)	0.3147 (6)	0.1218 (5)	0.067 (4)
N(41)	0.176 (1)	0.3534 (7)	0.2265 (7)	0.087 (5)
N(42)	0.291 (1)	0.3920 (6)	0.2457 (6)	0.073 (4)
C(10)	0.404 (1)	0.6101 (9)	0.0442 (7)	0.106 (5)
C(13)	0.251 (1)	0.635 (1)	0.2171 (7)	0.082 (5)
C(14)	0.250 (1)	0.727 (1)	0.193 (1)	0.100 (6)
C(15)	0.310 (1)	0.739 (1)	0.1256 (8)	0.101 (5)
C(20)	0.609 (2)	0.533 (1)	0.0750 (7)	0.153 (8)
C(23)	0.623 (1)	0.4827 (8)	0.2644 (7)	0.088 (5)
C(24)	0.748 (2)	0.519 (1)	0.257 (1)	0.130 (6)
C(25)	0.758 (1)	0.548 (1)	0.1845 (9)	0.117 (6)
C(30)	0.245 (1)	0.3008 (9)	0.0627 (6)	0.091 (6)
C(33)	0.553 (1)	0.257 (1)	0.1319 (7)	0.097 (6)
C(34)	0.529 (2)	0.164 (1)	0.1063 (8)	0.110 (6)
C(35)	0.408 (2)	0.1663 (9)	0.0792 (7)	0.091 (5)
C(40)	0.115 (1)	0.3847 (8)	0.1593 (9)	0.095 (5)
C(43)	0.317 (1)	0.3590 (8)	0.3142 (7)	0.090 (5)
C(44)	0.208 (2)	0.304 (1)	0.3365 (9)	0.127 (8)
C(45)	0.121 (2)	0.300 (1)	0.280 (1)	0.130 (8)
*F(51)	0.089 (1)	0.5403 (6)	0.0214 (8)	0.22 (1)
*F(52)	-0.074 (1)	0.5696 (6)	-0.0486 (5)	0.168 (5)
*F(53)	0.063 (1)	0.6817 (6)	-0.0193 (7)	0.176 (6)
*F(54)	-0.068 (1)	0.628 (1)	0.0596 (7)	0.33 (2)
*B(50)	0.002 (1)	0.6042 (8)	0.0026 (7)	0.24 (2)
F(61)	0.8516 (6)	0.0668 (5)	0.0819 (4)	0.147 (4)
F(62)	1.0492 (8)	0.1116 (6)	0.0640 (4)	0.189 (5)
F(63)	0.9780 (8)	0.0794 (9)	0.1734 (4)	0.271 (8)
F(64)	0.915 (1)	0.2066 (6)	0.1200 (7)	0.250 (8)
B(60)	0.949 (1)	0.1156 (8)	0.1090 (5)	0.26 (2)

to the disorder and high thermal motion of the BF₄ anions that could be described only partially with the adopted parameter model. The absolute structure was determined with final refinements of the structure with positive and negative f'' values respectively, resulting in a slightly lower R value ($\Delta R = 0.01$) for the final positions that appear in Table 1.* A final difference Fourier map did not show residual peaks outside $\pm 0.48 \text{ e } \text{Å}^{-3}$. Scattering factors of Cromer & Mann (1968) and anomalous-dispersion terms from Cromer & Liberman (1970) were used. Most calculations were carried out on a Microvax II. The program *PLATON* (Spek, 1982) was used for the calculation of the geometrical data.

Discussion. The orthorhombic unit cell contains four Ni-complex cations and eight BF₄ anions. The Ni^{II} ion (Fig. 1) is surrounded by four azole nitrogens and two

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, parameters for the minor disorder component and geometrical data concerning H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44624 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

amine nitrogens of the two am₂p ligands. The geometry around the Ni^{II} ion (Table 2) is almost octahedral. The deviation from regular octahedral geometry is obviously imposed by the ligands in which the three ligand bonds from the pyrazole N to the amine N form too short a bridge to allow for a pyrazole-nitrogen to Ni to amine-nitrogen angle of 90°. This restricted angle of about 80° also occurs in analogous compounds (Hulsbergen, Driessen, Reedijk & Verschoor, 1984; van Driel, Driessen & Reedijk, 1985; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985). Distances from the Ni ion to the azole nitrogens lie in the narrow range of 2.02–2.07 Å, the distances to the amine nitrogens are slightly larger, about 2.18 Å. Fig. 1 clearly shows that the two ligand molecules are in a *fac* configuration. The ligands are also hydrogen bonded, through the H atom on the amine N, to the anions with an N(2)···F(51) distance of 2.82 (1) Å and a bifurcated bond with N(1)···F(62) 2.97 and N(1)···F(61) 3.11 (1) Å. These distances are rather long, which is also reflected in the occurrence of the N–H stretching vibration band at 3300 cm⁻¹, indicating a rather weak hydrogen bond to the fluoroborate ions (Bellamy & Owen, 1969). The weakness of the hydrogen bond is also reflected by the disorder in the positions of the fluorine atoms, as strong hydrogen bonding usually prevents such disorder from occurring. The splitting off of a pyrazole group from the ligand tris(1-pyrazolylmethyl)amine and the subsequent formation of the [Ni(am₂p)₂]²⁺ cation has apparently not been induced by an extra stability gain through hydrogen-bond formation to the anions, but may rather have been induced by the preference of Ni^{II} for octahedral coordination. The pyrazole rings are planar with distances to the least-squares planes not exceeding 0.02 (8) Å. The molecules pack, apart from H bonding, with no abnormally short intermolecular contacts. There is no intermolecular stacking of the aromatic ring.

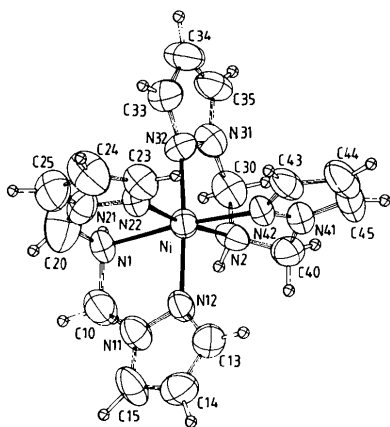


Fig. 1. ORTEP (Johnson, 1970) drawing of the Ni^{II} cation. The surfaces have been drawn at the 40% probability level.

Table 2. Bond distances (Å) and bond angles (°) for the non-H atoms

Ni–N(1)	2.182 (9)	N(31)–C(30)	1.44 (1)
Ni–N(2)	2.17 (1)	N(31)–C(35)	1.34 (2)
Ni–N(12)	2.038 (7)	N(32)–C(33)	1.31 (2)
Ni–N(22)	2.02 (1)	N(41)–N(42)	1.34 (1)
Ni–N(32)	2.028 (9)	N(41)–C(40)	1.43 (2)
Ni–N(42)	2.07 (1)	N(41)–C(45)	1.34 (2)
N(1)–C(10)	1.48 (1)	N(42)–C(43)	1.34 (2)
N(1)–C(20)	1.37 (2)	C(13)–C(14)	1.34 (2)
N(2)–C(30)	1.43 (1)	C(14)–C(15)	1.37 (2)
N(2)–C(40)	1.48 (2)	C(23)–C(24)	1.38 (2)
N(11)–N(12)	1.32 (1)	C(24)–C(25)	1.37 (2)
N(11)–C(10)	1.44 (2)	C(33)–C(34)	1.38 (2)
N(11)–C(15)	1.35 (2)	C(34)–C(35)	1.33 (3)
N(12)–C(13)	1.34 (2)	C(43)–C(44)	1.41 (2)
N(21)–N(22)	1.32 (1)	C(44)–C(45)	1.35 (3)
N(21)–C(20)	1.44 (2)	N(22)–C(23)	1.33 (2)
N(21)–C(25)	1.34 (2)	N(31)–N(32)	1.33 (1)
N(1)–Ni–N(2)	99.8 (4)	N(32)–N(31)–C(35)	112 (1)
N(1)–Ni–N(12)	79.0 (4)	C(30)–N(31)–C(35)	128 (1)
N(1)–Ni–N(22)	79.5 (4)	Ni–N(32)–N(31)	115.4 (7)
N(1)–Ni–N(32)	92.8 (4)	Ni–N(32)–C(33)	139.7 (9)
N(1)–Ni–N(42)	173.8 (3)	N(31)–N(32)–C(33)	103.8 (9)
N(2)–Ni–N(12)	93.5 (3)	N(42)–N(41)–C(40)	119 (1)
N(2)–Ni–N(22)	171.6 (4)	N(42)–N(41)–C(45)	114 (1)
N(2)–Ni–N(32)	79.2 (4)	C(40)–N(41)–C(45)	126 (1)
N(2)–Ni–N(42)	80.2 (4)	Ni–N(42)–N(41)	111.3 (8)
N(12)–Ni–N(22)	94.5 (4)	Ni–N(42)–C(43)	139.6 (8)
N(12)–Ni–N(32)	168.0 (4)	N(41)–N(42)–C(43)	106 (1)
N(12)–Ni–N(42)	98.8 (4)	N(1)–C(10)–N(11)	109 (1)
N(22)–Ni–N(32)	92.5 (4)	N(12)–C(13)–C(14)	106 (1)
N(22)–Ni–N(42)	101.4 (4)	C(13)–C(14)–C(15)	113 (1)
N(32)–Ni–N(42)	93.3 (4)	N(11)–C(15)–C(14)	100 (1)
Ni–N(1)–C(10)	108.1 (7)	N(1)–C(20)–N(21)	115 (1)
Ni–N(1)–C(20)	108.8 (7)	N(22)–C(23)–C(24)	110 (1)
C(10)–N(1)–C(20)	116.2 (9)	C(23)–C(24)–C(25)	105 (1)
Ni–N(2)–C(30)	110.3 (7)	N(21)–C(25)–C(24)	106 (1)
Ni–N(2)–C(40)	105.2 (7)	N(2)–C(30)–N(31)	112.0 (9)
C(30)–N(2)–C(40)	116.6 (8)	N(32)–C(33)–C(34)	112 (1)
N(12)–N(11)–C(10)	119 (1)	C(33)–C(34)–C(35)	105 (1)
N(12)–N(11)–C(15)	114 (1)	N(31)–C(35)–C(34)	106 (1)
C(10)–N(11)–C(15)	126 (1)	N(2)–C(40)–N(41)	108.6 (9)
Ni–N(12)–N(11)	115.3 (7)	N(42)–C(43)–C(44)	107 (1)
Ni–N(12)–C(13)	136.5 (8)	C(43)–C(44)–C(45)	109 (1)
N(11)–N(12)–C(13)	107.0 (9)	N(41)–C(45)–C(44)	104 (2)
N(22)–N(21)–C(20)	119 (1)	Ni–N(22)–C(23)	139.9 (8)
N(22)–N(21)–C(25)	112 (1)	N(21)–N(22)–C(23)	105.4 (9)
C(20)–N(21)–C(25)	128 (1)	N(32)–N(31)–C(30)	119 (1)
Ni–N(22)–N(21)	114.6 (8)		

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Structure of Bis(di-*O*-propyl 1-cyano-2-oxopropylphosphonato)copper(II)

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Abstract. [Cu(C₁₀H₁₇NO₄P)₂], $M_r = 555.99$, monoclinic, $P2_1/c$, $a = 10.588$ (2), $b = 13.395$ (3), $c = 9.540$ (5) Å, $\beta = 90.32$ (3)°, $V = 1353$ (1) Å³, $Z = 2$, $D_x = 1.365$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 9.7$ cm⁻¹, $F(000) = 582$, $T = 292$ K, $R = 0.075$ for 1738 observed reflections. The structure consists of centrosymmetric CuL₂ molecules, $L = \text{CH}_3\text{COC}(\text{CN})\text{PO}(\text{OC}_3\text{H}_7)_2$, associated in infinite layers parallel to (001). The coordination of the Cu atom is an elongated rhombic octahedron of four O atoms at 1.948 (7) and 1.958 (7) Å and two N atoms from two adjacent CuL₂ units at 2.516 (5) Å. The ligands L perform both chelating (O=C–C–P=O fragment) and intermolecular-linking (C≡N groups) functions. The propoxy groups in the crystal lattice are poorly located.

Introduction. IR spectroscopic studies of several metal complexes with dialkoxyphosphonyl acetones (dapac) suggested that their coordination properties resembled those of 1,3-diketones (Petrov, 1972). X-ray structure analysis of Mg₃(acac)₆ (acac = acetylacetonate) along with Mg₃(depac)₆ (depac = diethoxyphosphonyl acetone) (Weiss, Kopf, Gardein, Corbelin, Schuman, Kirilov & Petrov, 1985) corroborated this suggestion. The introduction of a cyano group into the α -position relative to the P=O group in dapac creates a new coordinating site and the ligand becomes potentially tridentate. Earlier the chelation of copper by 1-cyano-2-oxopropylphosphonic acid dipropyl ester was unequivocally established by IR investigations (Petrov & Kirilov, 1968) but before the present work it was difficult to ascertain the structural role of the C≡N group.

Experimental. Crystals obtained by recrystallization from an ether solution of the complex synthesized as described by Petrov & Kirilov (1968). A light-green prismatic crystal with approximate dimensions 0.12 × 0.17 × 0.22 mm investigated. D_m not determined. Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); $\omega/2\theta$ scan: speed 2 to 10° min⁻¹, width = (0.9 + 0.350 tan θ)°. Cell constants from least-squares refinement of 22 reflections with $22 < \theta < 24$ °. 5888 reflections measured in range of $(\sin \theta)/\lambda < 0.616$ Å⁻¹ ($h: 0$ to 11, $k: 0$ to 16, $l: -13$ to 13 and their Friedel equivalents). Three standard reflections (monitored every 2.0 h), intensity variation < 0.1%. No decay correction. Lorentz and polarization correction; empirical absorption correction, transmission factors varied from 0.935 to 0.999. 1806 unique reflections with $R_{\text{int}} = 0.016$; 2126 reflections considered unobserved [$I < 3\sigma(I)$]. Structure solved by heavy-atom method and refined by restrained least squares on F^2 s (program *LSRE*, restraints applied to propoxy groups with distances for O–C = 1.35, C–C = 1.54 Å and angles at C atoms of 109.5°). Attempts to determine any disorder scheme were unsuccessful. H atoms not included in refinements. Final $R = 0.050$, $wR = 0.065$ and $S = 6.017$ for 1530 observed reflections with $|F_o - |F_c|| < 9\sigma(F_o)$; $R = 0.075$, $wR = 0.128$ for all 1738 observed reflections; weights w defined as $4F_o^2/[\sigma^2(F_o)]^2$. Max. $(\Delta/\sigma) = 0.19$; max. residual density ± 1.0 e Å⁻³. Empirical correction for secondary extinction, $F_{\text{corr}} = F/(1+gI)$ with $g = 0.774 \times 10^{-6}$. Atomic scattering factors and anomalous-dispersion coefficients from *SDP/PDP V3.0* software package (Enraf–Nonius, 1985) used for