

## A Copper–Nitromalonamide Complex

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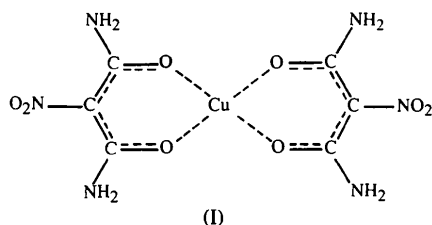
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## Abstract

Bis(2-nitromalonamide-*O,O'*)copper(II), [Cu{O<sub>2</sub>NC(C—ONH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>], is a neutral complex. The Cu atom is octahedrally coordinated to six O atoms from four ligands and is situated on a centre of symmetry. Each ligand coordinates to the Cu atom *via* relatively short bonds from the amide O atoms. Weak bonds to Cu originate from one of the O atoms of the nitro group. The Cu complex is bent around lines 'drawn' through the amide O atoms of each ligand.

## Comment

In a continuation of our study of nitromalonamide and its NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> salts (Simonsen & Thorup, 1979; Simonsen, 1981), we decided to investigate nitromalonamide as a ligand. Accordingly, we have prepared a Cu complex with the nitromalonamide anion as a ligand, (I), and determined its crystal structure.



(I)

The structure is described in terms of a monoclinic cell in which the *a* and *c* axes are of equal length, within experimental error, and transformation to a *C*-centered orthorhombic cell is therefore possible. However, the *mmm* Laue symmetry associated with an orthorhombic reciprocal lattice was not observed for (I) when a comparison was made among symmetry-related reflections after transformation to the orthorhombic setting. Consequently, the structure has been assigned the monoclinic space group *P*2<sub>1</sub>/*a*.

The planar configuration of nitromalonamide is stabilized by an intramolecular O—H···O hydrogen bond between the amide O atoms. During salt formation, the H atom in this hydrogen bond is lost and the nitromalonamide anion becomes a non-planar system with one of the amide groups rotated out of the molecular plane by approximately 75°.

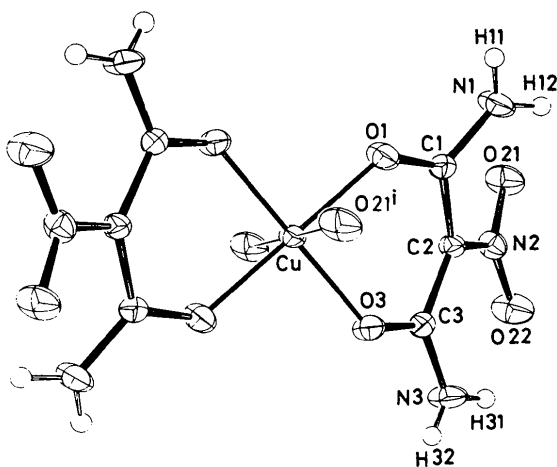


Fig. 1. Displacement ellipsoid plot of (I) with ellipsoids drawn at the 50% probability level [symmetry code: (i) *x*, *y*, 1 + *z*].

On complex formation the Cu atom in (I) coordinates to the amide O atoms and thereby maintains a less twisted configuration of the ligand, with the torsion angles O1—C1—C2—C3 24.6 (3) and C1—C2—C3—O3 −15.5 (3)° compared to −4.61 (4) and −68.9 (4)°, respectively, for the corresponding angles in the NH<sub>4</sub><sup>+</sup> salt of nitromalonamide. Noteworthy changes in (I) compared to the NH<sub>4</sub><sup>+</sup> salt of nitromalonamide (Table 3) are elongation of C2—N2, C3—O3 and C1—O1, and shortening of N2—O21, N2—O22 and C2—C3; the last of these bonds is now the same length as C1—C2. From these bond-length changes, we conclude that negative charge is displaced from the nitro group to the amide O atoms.

According to the criteria of Görbitz (1989), the intramolecular hydrogen bonds N3—H31···O22 [N3···O22 2.557, H31···O22 1.95 (2) Å] and N1—H12···O21 [N1···O21 2.661 (3), H12···O21 2.24 (2) Å] are relatively strong and rather weak, respectively. This is also reflected in a more planar arrangement for N3, C3, C2, N2 and O22 compared to N1, C1, C2, N2 and O21: the maximum deviations from the respective least-squares planes defined by these two sets of atoms are 0.057 (3) and 0.215 (3) Å.

Square-planar CuO<sub>4</sub> coordination combined with relatively weak axial Cu···O contacts is often observed (Chingi, Guastini, Musatti & Nardelli, 1969; Prout *et al.*, 1968). The Cu—O coordination distances are quoted in Table 2. The distances compare well with those found in bis(hydrogen *o*-phthalato)diaquacopper(II) [Cu—O 1.930 (8), 1.967 (8) and 2.677 (5) Å; Chingi, Guastini, Musatti & Nardelli, 1969]. The O—Cu—O coordination angles in (I) are within the range 90±6.5°. (I) is folded around lines through the amide O atoms O1 and O3, the dihedral angle between the least-squares plane through Cu, O1 and O3 and that through O1, C1, C2, C3 and O3 being 30.81 (9)°. The nitro group con-

tributes to stabilization of the crystal structure through a weak  $\text{Cu}\cdots\text{O21}^{\text{i}}$  contact [symmetry code: (i)  $x, y, z - 1$ ] and an intermolecular  $\text{N1}\cdots\text{O22}^{\text{ii}}$  hydrogen bond [2.894 (2) Å; symmetry code: (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$ ].

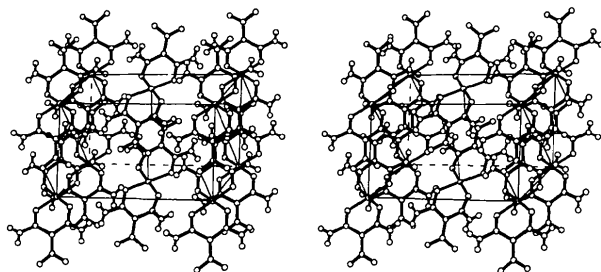


Fig. 2. Stereodrawing (ATOMS2.2; Dowty, 1992) of the unit cell of (I) with the  $y$  axis horizontal and the  $z$  axis vertical.

## Experimental

A solution was prepared by dissolving nitromalonamide in excess aqueous ammonia (25%,  $\text{NH}_3$ ). 0.5M  $\text{CuSO}_4(\text{aq})$  was added. Suitable crystals of (I) separated from the solution by room-temperature evaporation. The density  $D_m$  was measured by flotation in a mixture of  $\text{CH}_3\text{I}$  and  $\text{CH}_2\text{ClBr}$ .

### Crystal data

$[\text{Cu}(\text{C}_3\text{H}_4\text{N}_3\text{O}_4)_2]$   
 $M_r = 355.71$   
 Monoclinic  
 $P2_1/a$   
 $a = 6.922(1) \text{ \AA}$   
 $b = 12.297(1) \text{ \AA}$   
 $c = 6.922(1) \text{ \AA}$   
 $\beta = 113.85(1)^\circ$   
 $V = 539.0(3) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 2.192 \text{ Mg m}^{-3}$   
 $D_m = 2.16(1) \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 18 reflections  
 $\theta = 11.37\text{--}14.14^\circ$   
 $\mu = 2.06 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prism (cut)  
 $0.39 \times 0.33 \times 0.16 \text{ mm}$   
 Blue-green

### Data collection

Enraf-Nonius CAD-4F diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: by integration from crystal shape  
 $T_{\min} = 0.54, T_{\max} = 0.74$   
 1564 measured reflections  
 1564 independent reflections

1416 observed reflections  
 $[F > 2.5\sigma(F)]$   
 $\theta_{\max} = 29.97^\circ$   
 $h = 0 \rightarrow 9$   
 $k = 0 \rightarrow 17$   
 $l = -9 \rightarrow 8$   
 3 standard reflections frequency: 180 min intensity decay: 1%

### Refinement

Refinement on  $F^2$   
 $R = 0.027$   
 $wR = 0.027$   
 $S = 7.678$

$(\Delta/\sigma)_{\max} = 0.134$   
 $\Delta\rho_{\max} = 0.4 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.5 \text{ e \AA}^{-3}$   
 Extinction correction: none

1416 reflections  
 109 parameters  
 Four H atoms located from  $\Delta\rho$  map; only coordinates refined  
 $w = 1/\sigma^2(F)$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Cu	1/2	1/2	0	0.0207 (2)
C1	0.2464 (3)	0.4227 (2)	0.2109 (3)	0.0194 (9)
C2	0.2549 (3)	0.5313 (1)	0.3016 (3)	0.0178 (8)
C3	0.2833 (3)	0.6273 (2)	0.1913 (3)	0.0186 (8)
N1	0.1419 (4)	0.3430 (2)	0.2528 (3)	0.030 (1)
N2	0.2274 (3)	0.5424 (1)	0.4879 (3)	0.0224 (8)
N3	0.2432 (4)	0.7261 (1)	0.2406 (3)	0.030 (1)
O1	0.3315 (3)	0.4025 (1)	0.0837 (2)	0.0295 (8)
O21	0.2382 (3)	0.4606 (1)	0.6022 (2)	0.0307 (8)
O22	0.2010 (3)	0.6346 (1)	0.5531 (2)	0.0349 (8)
O3	0.3466 (2)	0.6197 (1)	0.0428 (2)	0.0233 (7)

Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

Cu—O1	1.918 (2)	Cu $\cdots$ O21 <sup>i</sup>	2.658 (1)
Cu—O3	1.907 (2)		
O1—Cu—O3	89.47 (7)	C1—C2—C3	120.2 (2)
Cu—O1—C1	126.8 (1)	C2—C3—O3	121.7 (2)
Cu—O3—C3	125.2 (1)	O1—Cu $\cdots$ O21 <sup>i</sup>	87.49 (6)
C2—C1—O1	121.8 (2)	O3—Cu $\cdots$ O21 <sup>i</sup>	96.46 (5)

Symmetry code: (i)  $x, y, z - 1$ .

Table 3. Bond lengths ( $\text{\AA}$ ) in the ligand of (I) compared with corresponding bond lengths in related compounds

	(I) <sup>a</sup>	$\text{NH}_4^+\text{C}_3\text{H}_4\text{N}_3\text{O}_4^-$ <sup>b</sup>	$\text{C}_3\text{H}_5\text{N}_3\text{O}_4^-$ <sup>c</sup>
O1—C1	1.266 (3)	1.253 (4)	1.302 (4)
O3—C3	1.273 (3)	1.241 (4)	1.281 (4)
O21—N2	1.263 (2)	1.286 (4)	1.244 (3)
O22—N2	1.261 (3)	1.300 (4)	1.249 (4)
N1—C1	1.318 (3)	1.336 (4)	1.301 (4)
N2—C2	1.385 (3)	1.327 (4)	1.397 (4)
N3—C3	1.321 (3)	1.327 (4)	1.322 (5)
C1—C2	1.467 (3)	1.468 (4)	1.447 (5)
C2—C3	1.462 (3)	1.500 (4)	1.456 (4)

References: (a) this work; (b) Simonsen (1981); (c) Simonsen & Thorup (1979).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1982). Cell refinement: *CAD-4 Software*. Data reduction: Norrestam & Nielsen (1982); *ADDREF, SORTRF* in *Xtal3.2* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYLSQ* in *Xtal3.2*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *Xtal3.2*; *ATOMS2.2* (Dowty, 1992). Software used to prepare material for publication: *Xtal3.2*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1175). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Bis[tricarbonyl(triisopropyl phosphite)-cobalt](Co—Co) Dichloromethane Solvate

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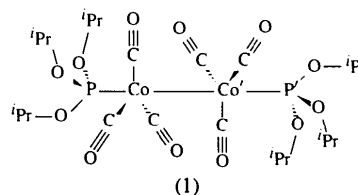
## Abstract

The complex of the title compound, [Co<sub>2</sub>(CO)<sub>6</sub>(C<sub>9</sub>H<sub>21</sub>O<sub>3</sub>P)<sub>2</sub>].CH<sub>2</sub>Cl<sub>2</sub>, lies about an inversion centre and displays trigonal bipyramidal coordination geometry about each Co atom, with axial phosphite ligands *trans* to the Co—Co bond. The Co—Co bond length of 2.6544(12) Å in this structure is shorter than Co—Co bond lengths reported for analogous phosphine complexes.

## Comment

The  $\sigma \rightarrow \sigma^*$  transition in dimetallic carbonyl complexes containing unsupported metal–metal bonds occurs in the visible or near-UV region of the spectrum and provides

a quantitative measure of the strength of the metal–metal interaction in these complexes (Levenson, Gray & Ceasar, 1970; Levenson & Gray, 1975; Abrahamson *et al.*, 1977). We have obtained more data for the energies of the  $\sigma \rightarrow \sigma^*$  transition in the metal–metal-bonded complexes [Mn<sub>2</sub>(CO)<sub>8</sub>L<sub>2</sub>] and [Co<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub>] (*L* is a P-donor ligand) and it is clear that the trends cannot be accounted for on the basis of  $\sigma$ -donicity,  $\pi$ -acidity and steric effects, as had been concluded on the basis of the less complete data. To gain more insight into the metal–metal interactions in these complexes, we undertook the crystal structure determination of the complex [Co<sub>2</sub>(CO)<sub>6</sub>{P(O<sup>*i*</sup>Pr)<sub>3</sub>}<sub>2</sub>], (1).



The title complex possesses a crystallographically imposed centre of inversion halfway along the Co—Co bond. Each Co atom has the same slightly distorted trigonal bipyramidal arrangement with three carbonyl ligands in the equatorial plane, an axial Co atom and an axial phosphite ligand. The angles subtended at the Co atom in the equatorial plane range from 118.8(2) to 120.7(2)°, with the sum of the three angles being 358.9(1)°. The axial P—Co—Co' angle is 177.00(6)°. The presence of the inversion centre at the midpoint of the Co—Co bond ensures that the carbonyl groups attached to the Co atoms adopt a fully staggered conformation. All the carbonyl groups are essentially linear [Co—C—O angles are statistically equivalent with an average value of 176.7(6)°]. The three O atoms in each phosphite ligand are disordered, each appearing in two positions with site occupancies of 0.5. All distances and angles associated with the phosphite ligands are normal (Allen *et al.*, 1987). The asymmetric unit contains one-half of a disordered dichloromethane solvent molecule. The presence of CH<sub>2</sub>Cl<sub>2</sub> is consistent with the <sup>1</sup>H NMR spectrum of a solution of the crystals in CDCl<sub>3</sub>.

The most interesting feature of the structure is the presence of a non-bridged metal–metal bond. Selected geometric parameters for the complexes [Co<sub>2</sub>(CO)<sub>6</sub>L<sub>2</sub>] are presented in Table 3, where *L* = P(O<sup>*i*</sup>Pr)<sub>3</sub> (1), P(<sup>*n*</sup>Bu)<sub>3</sub> (Ibers, 1968), PMe<sub>3</sub> (Jones, Seeberger, Stuart, Whittlesey & Wright, 1986) and PPh<sub>2</sub>[C<sub>2</sub>(Me<sub>2</sub>As)(CF<sub>2</sub>)<sub>2</sub>] (Einstein & Kirkland, 1978). The Co—Co and Co—P distances in the three previously reported phosphine structures are equivalent for each type and average 2.666(2) and 2.175(1) Å, respectively. The Co—Co bond length in (1), 2.6544(12) Å, is significantly shorter (9σ) than the values observed in the phosphine-substituted Co—Co dimeric complexes. The