Lists of structure factors, anisotropic thermal parameters and complete bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71075 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1017]

References

Anderson, O. P. (1975). *Inorg. Chem.* **14**, 730–734.
Berry, R. S. (1960). *J. Chem. Phys.* **32**, 933–938.
Dunaj-Jurčo, M., Ondrejovič, G., Melník, M. & Garaj, J. (1988). *Coord. Chem. Rev.* **83**, 1–28.
Dyason, J. C., Healy, P. C., Engelhardt, L. M., Pakawatchai, C., Patrick, V. A. & White, A. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 839–844.
Harrison, W. D. & Hathaway, B. J. (1980). *Acta Cryst.* B**36**, 1069–1074, and references therein.
Morpurgo, G. O., Dessy, G. & Fares, V. (1984). *J. Chem. Soc. Dalton Trans.* pp. 785–791.
NRC Crystallographic Programs for the IBM360 System (1973). Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.
Vaira, M. D. & Mani, F. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2327–2332.

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Mixed-Valence Cu^I–Cu^{II} Complexes. Structure of Cyanobis(1,10-phenanthroline)copper(II) Bis(cyano)(1,10-phenanthroline)cuprate(I) Pentahydrate

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Abstract

Reaction of $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline) and KCN in the molar ratio 1:40:2:2 in water–ethanol solution gives a new mixed-valence complex of composition $Cu_2(phen)_3(CN)_3.5H_2O$. X-ray structure analysis reveals the composition $[Cu^{II}(phen)_2(CN)]^+[Cu^I(phen)(CN)_2]^-.5H_2O$ with trigonal-bipyramidal and tetrahedral coordination for the divalent and univalent Cu atoms, respectively. The structure is built up of hydrated clusters comprising two formula units; the principal interactions within the cluster are hydrogen bonds between the water molecules and complex cations and anions.

Comment

This work is part of a project exploring the structural and chemical properties of mixed-valence copper complexes with organic and inorganic ligands. We have shown (Dunaj-Jurčo, Ondrejovič, Melník & Garaj, 1988) that all known Cu^I–Cu^{II} complexes can be subdivided into four groups according to the environment of the Cu^I and Cu^{II} atoms and their crystallostructural function. The title compound belongs to the first group containing Cu^I anion and Cu^{II} cation species; there are several routes for the preparation of this type of compound. In this work we have chosen that which utilizes CN^- ions both as a reducing agent (to reduce Cu^{II} to Cu^I) and as a ligand coordinated to Cu^{II} and Cu^I. Previously, Wicholas & Wolford (1974) reported that Cu^{II} compounds in which the CN^- ligand is directly bonded to Cu^{II} are relatively rare; these authors have also described the preparation of $Cu_2(phen)_3(CN)_3.6H_2O$. The title compound, $Cu_2(phen)_3(CN)_3.5H_2O$, was prepared in a similar way: 1 *M* aqueous solution of $Cu(NO_3)_2$ (10 ml), 26% NH_3 (30 ml), 1,10-phenanthroline monohydrate (3.6 g, 20 mmol) and ethanol (140 ml) were mixed; on dropwise addition of 1 *M* aqueous solution of KCN (20 ml) a violet non-crystalline precipitate formed; the mixture was allowed to stand for 7 d at room temperature, which yielded well shaped dark-green crystals. Since the crystals were unstable and cracked in air, they were sealed in epoxide for data collection.

The crystal structure was found to consist of discrete $[Cu^{II}(phen)_2CN]^+$ cations and $[Cu^I(phen)(CN)_2]^-$ anions held together by hydrogen-bonded water molecules. An *ORTEP* (Johnson, 1965) view of the cation and anion is shown in Fig. 1.

The complex cation exhibits approximately trigonal-bipyramidal coordination geometry about the Cu^{II} ion, with the cyanide ion occupying an equatorial position. The bond angles in the equatorial plane are considerably distorted from the ideal trigonal angle of 120°, with two large angles of 132.8 (6) (α_1 = C1—Cu—N13) and 123.3 (5)° (α_2 = C1—Cu—N12), and one small angle of 103.9 (5)° (α_3 = N12—Cu—N13). The distance of the Cu^{II} atom from the plane (C1, N12, N13) is 0.016 (8) Å,

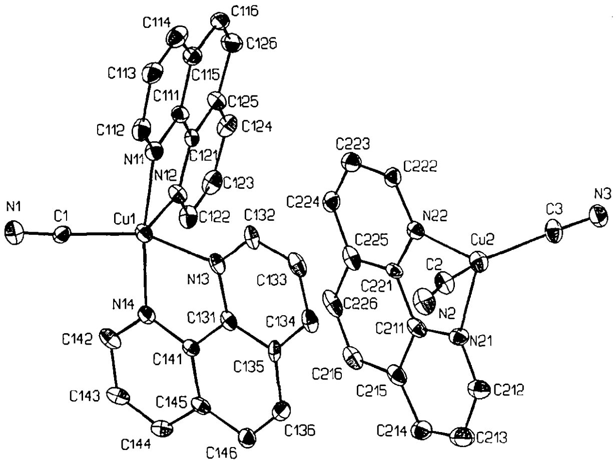

Fig. 1. *ORTEP* drawing of the complex cation and anion. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

indicating coplanarity of the Cu^{II} ion with the three coordinating atoms. The axial Cu—N bond lengths [1.966 (9) and 1.969 (9) Å] are equivalent and significantly shorter than the equatorial Cu—N bond distances; however, the latter differ from one another by a significant amount [*ca* 10σ; 2.128 (7) and 2.046 (10) Å].

Similar sterochemical features for the cupric ion have been observed in other complexes containing the trigonal-bipyramidal $[Cu^{II}(phen)_2CN]^+$ moiety, namely, in monomeric $[Cu(phen)_2CN]NO_3.H_2O$ (Anderson, 1975) and dimeric mixed-valence $[Cu_2(phen)_3(CN)\{(Se,S)CN\}][(Se,S)CN].0.5EtOH$ (Dunaj-Jurčo, Kabešová, Kettman, Císařová & Mikloš, 1993), although in the latter two complexes the non-equivalence of the equatorial Cu—N bonds was not observed. On the other hand, replacement of the rigid phen ligand by a more flexible ligand in the complex $[Cu_2([14]\text{-}4,11\text{-diene-}N_4)_2CN](ClO_4)_3$ (Duggan, Jungst, Mann, Stucky & Hendrickson, 1974), with the CN^- also occupying an equatorial position, resulted in an interchange of the relative lengths of axial and equatorial Cu—N bonds (axial bonds longer than equatorial). However, movement of the CN^- ion from the equatorial to an axial position, as in $[Cu_2(2,2',2''\text{-triaminoethylamine})_2(CN)_2](BPh_4)_2$ (Duggan *et al.*, 1974), did not perturb the axial compression of the coordination polyhedron. These observations suggest that for trigonal-bipyramidal Cu^{II} complexes the precise coordination geometry is determined by the rigidity of the organic ligands and crystal forces (*e.g.*, nature of the counterion) rather than the $3d^9$ electronic distribution or the position of the CN^- ligand.

As suggested by Harrison & Hathaway (1980), the in-plane angular distortions can be used to identify the position of the CuN_4C chromophore along the Berry twist pathway which describes the interconversion between trigonal-bipyramidal and square-pyramidal stereochemistries. For the title cation, the in-plane bond angles satisfy the relations $\alpha_1 - \alpha_2 <$ 15° and $\alpha_3 = 95\text{–}130°$ ($\alpha_1 - \alpha_2 = 9.5$, $\alpha_3 = 103.9°$), which are characteristic for a pure trigonal-bipyramidal stereochemistry with near C_{2v} symmetry. This clearly demonstrates the stabilizing effect of the phen and CN^- ligands against square-pyramidal distortion of the trigonal-bipyramidal stereochemistry of the CuN_4C core in the present complex cation.

As expected, the coordination polyhedron around the cuprous ion is a distorted tetrahedron; the largest angular distortions involve the N21—Cu—N22 bond angle of 76.4 (5)°, as a result of the small N–N bite of the phen ligand, and the C2—Cu—C3 angle of 129.9 (7)°, resulting from the repulsion of the negatively charged CN^- ions. The bond lengths and angles involving the CN^- ions and the phen ligands in both complex ions are close to those observed in similar structures.

Packing is dominated by hydrogen bonds acting between the water molecules and the complex cations and anions, creating a hydrated cluster of composition corresponding to one formula unit. There are two other O···O contacts [O4···O3 2.726 (14) and O5···O1 2.729 (15) Å] which might correspond to hydrogen bonds, although the angles O—H···O are small [90 (4) and 101 (9)°, respectively]. If these are accepted, the crystal stucture could be described as consisting of 'dimeric' clusters of composition $\{[Cu^{II}(phen)_2(CN)][Cu^{I}(phen)(CN)_2](H_2O)_5\}_2$ (Fig. 2). These clusters are packed by Coulombic and van der Waals forces.

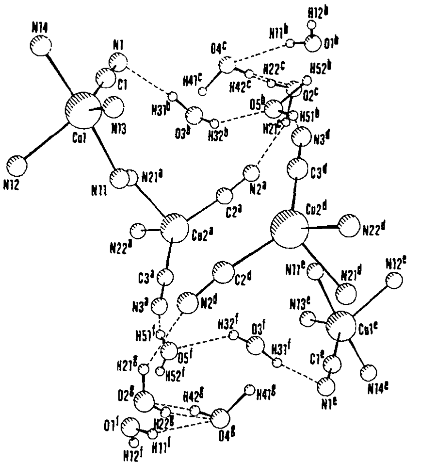

Fig. 2. Schematic drawing of hydrogen bonds formed within the 'dimeric' cluster comprising two formula units (see text).

Experimental

Crystal data

$[Cu(CN)(C_{12}H_8N_2)_2]$-$[Cu(CN)_2(C_{12}H_8N_2)]$.-$5H_2O$
M_r = 835.8
Triclinic
$P\bar{1}$
a = 11.483 (15) Å
b = 12.066 (15) Å
c = 15.586 (8) Å
α = 107.32 (10)°
β = 107.11 (9)°
γ = 106.79 (9)°
V = 1795 (4) Å^3
Z = 2
D_x = 1.546 Mg m^{-3}
D_m = 1.54 (1) Mg m^{-3}
Density measured by flotation in $CHBr_3$/acetone
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 15 reflections
θ = 6–15°
μ = 1.294 mm^{-1}
T = 293 K
Prism
0.7 × 0.4 × 0.3 mm
Dark green
Crystal source: crystallization from aqueous ethanol

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5123 measured reflections
4684 independent reflections
2658 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 22.5°
$h = -11 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections monitored every 100 reflections intensity variation: <5%

Refinement

Final R = 0.058
wR = 0.051
S = 1.61
2658 reflections
496 parameters
Only coordinates of H atoms refined
$w = 1.619/[\sigma^2(F_o) + 0.00054|F_o|^2]$
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\min}$ = −0.50 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
Cu1	0.2777 (1)	0.2604 (1)	0.2363 (1)	0.0516 (6)
Cu2	0.3549 (1)	−0.0068 (1)	0.6495 (1)	0.0608 (8)
N11	0.2963 (7)	0.1073 (7)	0.1636 (5)	0.0492 (43)
N12	0.0765 (6)	0.1227 (6)	0.1715 (5)	0.0506 (44)
N13	0.3586 (6)	0.2566 (6)	0.3706 (6)	0.0468 (41)
N14	0.2453 (7)	0.3976 (6)	0.3179 (6)	0.0475 (45)
N21	0.2829 (7)	0.1344 (7)	0.6895 (7)	0.0519 (46)
N22	0.2342 (6)	−0.0201 (7)	0.5135 (6)	0.0478 (45)
N1	0.3937 (8)	0.4069 (8)	0.1285 (7)	0.0751 (59)
N2	0.6426 (8)	0.1684 (9)	0.7172 (7)	0.0864 (69)
N3	0.2353 (9)	−0.2272 (8)	0.6946 (6)	0.0776 (58)
C1	0.3513 (9)	0.3555 (9)	0.1702 (7)	0.0541 (61)
C2	0.5388 (9)	0.0969 (10)	0.6881 (7)	0.0603 (63)
C3	0.2784 (9)	−0.1477 (10)	0.6756 (7)	0.0634 (65)
O1	0.0746 (7)	0.4918 (7)	0.8701 (6)	0.1130 (58)
O2	0.1683 (7)	0.6005 (6)	0.1373 (5)	0.0958 (49)
O3	0.4638 (7)	0.7060 (7)	0.9701 (6)	0.1019 (59)
O4	0.3164 (7)	0.5436 (7)	0.0260 (6)	0.1076 (55)
O5	0.2311 (8)	0.6689 (9)	0.8296 (7)	0.1388 (68)
C111	0.1865 (9)	−0.0023 (9)	0.1199 (6)	0.0466 (54)
C112	0.4053 (9)	0.1011 (9)	0.1575 (7)	0.0627 (55)
C113	0.4130 (11)	−0.0092 (13)	0.1106 (9)	0.0758 (82)
C114	0.3040 (13)	−0.1165 (11)	0.0667 (8)	0.0770 (82)
C115	0.1827 (11)	−0.1182 (10)	0.0691 (7)	0.0597 (32)
C116	0.0599 (13)	−0.2278 (9)	0.0259 (7)	0.0719 (67)
C121	0.0688 (8)	0.0079 (8)	0.1243 (6)	0.0422 (54)
C122	−0.0315 (10)	0.1345 (9)	0.1776 (7)	0.0603 (62)
C123	−0.1535 (9)	0.0293 (11)	0.1314 (8)	0.0653 (65)
C124	−0.1639 (9)	−0.0864 (10)	0.0833 (7)	0.0640 (61)
C125	−0.0503 (10)	−0.1013 (9)	0.0782 (7)	0.0548 (56)
C126	−0.0491 (10)	−0.2189 (9)	0.0315 (8)	0.0700 (66)
C131	0.3514 (8)	0.3456 (8)	0.4427 (8)	0.0442 (59)
C132	0.4163 (9)	0.1847 (8)	0.3964 (8)	0.0541 (62)
C133	0.4670 (9)	0.1970 (10)	0.4901 (10)	0.0677 (75)
C134	0.4605 (8)	0.2846 (9)	0.5634 (7)	0.0543 (56)
C135	0.4002 (8)	0.3620 (9)	0.5392 (8)	0.0469 (60)
C136	0.3845 (9)	0.4577 (10)	0.6072 (7)	0.0590 (60)
C141	0.2878 (8)	0.4193 (8)	0.4127 (8)	0.0429 (52)
C142	0.1855 (9)	0.4657 (9)	0.2877 (7)	0.0619 (59)
C143	0.1657 (9)	0.5556 (9)	0.3521 (9)	0.0687 (69)
C144	0.2083 (9)	0.5787 (8)	0.4468 (9)	0.0614 (66)
C145	0.2734 (8)	0.5100 (8)	0.4808 (8)	0.0473 (52)
C146	0.3243 (10)	0.5261 (9)	0.5786 (8)	0.0641 (64)
C211	0.2063 (9)	0.1477 (9)	0.6124 (9)	0.0524 (65)
C212	0.3147 (10)	0.2134 (11)	0.7774 (9)	0.0689 (73)
C213	0.2706 (13)	0.3086 (13)	0.7976 (10)	0.0930 (91)
C214	0.1945 (13)	0.3221 (10)	0.7245 (12)	0.0812 (79)
C215	0.1576 (9)	0.2418 (9)	0.6289 (10)	0.0598 (75)
C216	0.0742 (11)	0.2417 (10)	0.5397 (12)	0.0788 (82)
C221	0.1782 (8)	0.0629 (8)	0.5187 (8)	0.0416 (59)
C222	0.2117 (9)	−0.0969 (9)	0.4248 (9)	0.0523 (61)
C223	0.1319 (10)	−0.0967 (9)	0.3413 (7)	0.0588 (63)
C224	0.0728 (9)	−0.0168 (11)	0.3453 (8)	0.0599 (59)
C225	0.0970 (8)	0.0688 (9)	0.4360 (9)	0.0537 (60)
C226	0.0433 (8)	0.1599 (11)	0.4502 (10)	0.0689 (68)

Table 2. *Geometric parameters* (Å, °)

Cu1—N11	1.966 (9)	Cu2—N22	2.093 (9)
Cu1—N12	2.128 (7)	Cu2—C2	1.914 (10)
Cu1—N13	2.046 (10)	Cu2—C3	1.894 (13)
Cu1—N14	1.969 (9)	N1—C1	1.138 (17)
Cu1—C1	1.936 (13)	N2—C2	1.107 (12)
Cu2—N21	2.112 (10)	N3—C3	1.111 (16)
N14—Cu1—C1	95.4 (6)	C2—Cu2—C3	129.9 (7)
N13—Cu1—C1	132.8 (6)	N22—Cu2—C3	112.7 (6)
N13—Cu1—N14	80.6 (5)	N22—Cu2—C2	110.8 (6)
N12—Cu1—C1	123.3 (5)	N21—Cu2—C3	112.3 (6)
N12—Cu1—N14	95.0 (5)	N21—Cu2—C2	100.8 (6)
N12—Cu1—N13	103.9 (5)	N21—Cu2—N22	76.4 (5)
N11—Cu1—C1	93.4 (6)	Cu1—C1—N1	177.2 (12)
N11—Cu1—N14	171.1 (6)	Cu2—C2—N2	171.5 (13)
N11—Cu1—N13	93.9 (5)	Cu2—C3—N3	177.3 (11)
N11—Cu1—N12	79.4 (5)		

Data reduction: *XP*21 (Pavelčík, 1986). Structure refinement: *SHELX*76 (Sheldrick, 1976). Molecular geometry: *PARST* (Nardelli, 1983). Molecular graphics: *ORTEP* (Johnson, 1965); *MOLDRAW* (Ugliengo, Borzani & Viterbo, 1988).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles including those involving H atoms, and hydrogen-bond geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71121 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1018]

References

Anderson, O. P. (1975). *Inorg. Chem.* **14**, 730–734.
Duggan, D. M., Jungst, R. G., Mann, K. R., Stucky, G. D. & Hendrickson, D. N. (1974). *J. Am. Chem. Soc.* **96**, 3443–3450.

Dunaj-Jurčo, M., Kabešová, M., Kettman, V., Císařová, I. & Mikloš, D. (1993). *Acta Cryst.* C**49**, 1476–1479.
Dunaj-Jurčo, M., Ondrejovič, G., Melník, M. & Garaj, J. (1988). *Coord. Chem. Rev.* **83**, 1–28.
Harrison, W. D. & Hathaway, B. J. (1980). *Acta Cryst.* B**36**, 1069–1074.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pavelčík, F. (1986). *XP21*. Comenius Univ., Pharmaceutical Faculty, Bratislava, Czechoslovakia.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Ugliengo, P., Borzani, G. & Viterbo, D. (1988). *J. Appl. Cryst.* **21**, 75.
Wicholas, M. & Wolford, T. (1974). *Inorg. Chem.* **13**, 316–318.

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Structure of Bis(pentamethyldiethylenetriamine)disodium Hexasulfide

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Abstract

The new sodium sulfide compound, μ-hexasulfido-$1\kappa^2S^1,S^6{:}2\kappa^2S^1,S^6$-bis{[$N$-(dimethylaminoethyl)-$N,N'$,-$N'$-trimethyl-1,2-ethanediamine-κ^3N,N',N'']sodium}, $[Na(pmdeta)]_2[S_6]$ (1) [pmdeta = $(Me_2NCH_2CH_2)_2NMe$], was obtained by reacting two equivalents of sodium hydride with elementary sulfur in toluene containing an excess of pmdeta at approximately 238 K. The crystal structure contains a central Na_2S_2 ring in which both S atoms are part of an S_6^{2-} residue. In addition, each Na atom is coordinated by a pmdeta molecule.

Comment

The structure is a contact ion pair where the S_6^{2-} ion adopts a bent zigzag chain and the two Na^+ ions are both bridging the terminal S atoms. Thus a four-membered Na_2S_2 ring is formed. Furthermore, each Na atom is coordinated by a pmdeta molecule. Therefore, the overall structure is comparable to that of $[Li(tmeda)]_2[S_6]$ (tmeda = $Me_2NCH_2CH_2NMe_2$) (Banister, Barr, Brooker, Clegg, Cunnington, Doyle, Drake, Gill, Manning, Raithby, Snaith, Wade & Wright, 1990), but it is quite different from that of the ionic and acyclic polysulfides BaS_3, BaS_4, K_2S_5 and Ca_2S_6 (Wells, 1984). The four-membered Na_2S_2 ring is not planar; it is bent along the $Na1\cdots Na1^i$ vector. The normal of the $Na1$-$Na1^i$-S3 plane intersects that of the $Na1$-$Na1^i$-$S3^i$ plane with an angle of 19.80 (2)°. The bond lengths within the ring are 2.9073 (9) (Na1—S3) and 2.8245 (9) Å ($Na1—S3^i$). The bond distances in the S_6^{2-} chain are not of the same length. Whereas the terminal bonds are 2.0344 (7) (S2—S3) and 2.0487 (7) Å (S1—S2), the central $S1—S1^i$ bond is 2.1158 (9) Å long, hence 0.074 Å longer than the others. However, the average S—S bond length is in good agreement with the values for comparable derivatives, such as Cs_2S_6 (Abrahams & Grison, 1953) (average 2.054 Å) and $[Li(tmeda)]_2[S_6]$ (Tatsumi, Inoue, Nakamura, Cramer, VanDoorne & Gilje, 1990) (average 1.983 Å).

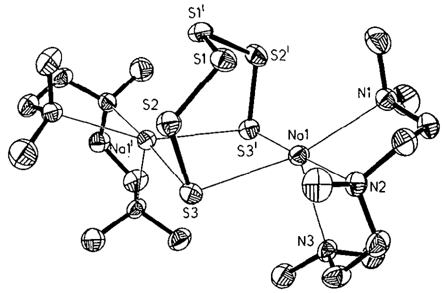

Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

Crystal data

$[Na_2(C_9H_{23}N_3)_2][S_6]$
M_r = 584.95
Tetragonal
$P\bar{4}2_1c$
a = 13.2390 (10) Å
c = 18.400 (2) Å
V = 3225.0 (5) Å^3
Z = 4
D_x = 1.205 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 64 reflections
θ = 10–12.5°
μ = 0.469 mm^{-1}
T = 293.0 (10) K
0.6 × 0.5 × 0.4 mm
Red

Data collection

Stoe Siemens AED four-circle diffractometer
Profile data from $2\theta/\omega$ scans
6917 measured reflections
3567 independent reflections
3273 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0304

$\theta_{\rm max}$ = 27.49°
$h = -14 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 90 min
intensity variation: none