

We thank Professor M. Nardelli for his interest in this work.

References

BRAIBANTI, A., MORI, G. & DALLAVALLE, F. (1978). *J. Chem. Soc. Dalton Trans.* In the press.

SHELDRIK, G. M. (1976). *SHELX*. Program for structure determination. Univ. of Cambridge, England.

WILHELM, E. & FISCHER, K. F. (1976a). *Cryst. Struct. Commun.* **5**, 511–514.

WILHELM, E. & FISCHER, K. F. (1976b). *Cryst. Struct. Commun.* **5**, 515–518.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

Acta Cryst. (1979). **B35**, 353–357

The Crystal and Molecular Structure of the 2:1 Salt Bis(*N*-methylphenazinium) Bis(maleodinitriledithiolato)nickelate(II), [(NMP)₂]²⁺[Ni(mnt)₂]²⁻

BY H. ENDRES,* H. J. KELLER, W. MORONI AND D. NÖTHE

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany

(Received 30 August 1978; accepted 10 November 1978)

Abstract

[(C₁₃H₁₁N₂)₂]²⁺[NiS₄C₄(CN)₄]²⁻, *M_r* = 729.6, crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 11.987 (5), *b* = 8.639 (4), *c* = 16.481 (13) Å, β = 106.05 (5)°, *V* = 1640 Å³, *Z* = 2, *d*_{calc} = 1.477 Mg m⁻³. The structure, including H, was solved by Patterson and Fourier methods and refined by least-squares calculations to *R* = 0.041, based on 1144 observations. Planar [Ni(mnt)₂]²⁻ anions are sandwiched between slightly bent (4°) [NMP]⁺ cations. The interplanar separation is 3.48 Å. The triads are stacked along *a* with an interplanar separation between adjacent triads of 3.35 Å and a very weak electronic overlap. The compressed pellet conductivity is 6 × 10⁻³ Ω⁻¹ m⁻¹.

Introduction

One of the systems of interest in the field of solids with 'low-dimensional' physical properties (Keller, 1977; Miller, 1978) are charge-transfer compounds consisting of planar organic donor molecules and planar transition-metal complexes as acceptors. The best suited transition-metal complexes appear to be bis(1,2-dithiolato) complexes of the nickel triad, which readily undergo electron-transfer reactions. Reviews of the properties of such complexes have been published by McCleverty (1968) and Eisenberg (1970). Some solids consisting of those anions and of nonconducting cations exhibit moderate to high electrical conductivities, up to 100 Ω⁻¹ m⁻¹ for compressed pellets (Perez-Albuérne, Isett & Haller, 1977). These high

conductivities imply the occurrence of a stacked structure of anions in the crystals. This kind of structure has been found in [(C₂H₅)₄N][Ni(mnt)₂] with a room-temperature resistivity of 3.5 × 10³ Ω m in the stack direction (Kobayashi & Sasaki, 1977), and in [(*n*-C₄H₉)₄N][Cu(mnt)₂] (Forrester, Zalkin & Templeton, 1964). Electrical conductivity has also been found in salts of bis(1,2-dithiolato) complexes with planar organic donors such as tetrathiafulvalene (TTF), *e.g.* (TTF)₂[*M*(mnt)₂], *M* = Cu, Co, Ni, Pt, and (TTF)-[Pt(mnt)₂], σ < 10⁻⁴ Ω⁻¹ m⁻¹ (Wudl, 1975); (TTF)-[Ni(mnt)₂], σ = 5 × 10⁻² Ω⁻¹ m⁻¹ (Wudl, Ho & Nagel, 1973); (TTF)₂[NiS₄C₄H₄], σ = 0.1 Ω⁻¹ m⁻¹ (Interrante, Browall, Hart, Jacobs, Watkins & Wee, 1975). With tetrathiatetracene (TTT) as a donor, observed conductivities were 30 Ω⁻¹ m⁻¹ for (TTT)₂-[Pt(mnt)₂] and 1 Ω⁻¹ m⁻¹ for (TTT)[Pt(mnt)₂] (Whealand & Gilson, 1976), and 3 × 10³ Ω⁻¹ m⁻¹ for (TTT)_{1,2}[NiS₄C₄H₄] (Interrante, Bray, Hart, Kasper, Piacente & Watkins, 1977). In (perylene)₂-[*M*(mnt)₂], *M* = Ni, Cu, Pd, single-crystal conductivities of 5 × 10³ Ω⁻¹ m⁻¹ have been detected (Alcacer & Maki, 1974), and the occurrence of stacks of perylene with a formal charge of ½ per molecule has been suggested. As one unit-cell axis is only 4.06 Å, the metal complexes should form stacks, too. Yet in all the complete structure determinations of salts of bis(1,2-dithiolato)metal complex anions and planar organic cations, no segregated stacks of anions and cations have been found. Stacks of alternating cations and anions occur in nonconducting (TTF)[CuS₄C₄(CF₃)₄] (Bray, Hart, Interrante, Jacobs, Kasper, Watkins, Wee & Bonner, 1975), and in semiconducting (σ = 10⁻³ Ω⁻¹ m⁻¹ for single crystals) 1:1 adducts of perylene and pyrene with NiS₄C₄(CF₃)₄ (Schmitt, Wing & Maki, 1969). Regular stacks of the donor have been

* To whom correspondence should be addressed.

found in $(\text{TTF})_{1,2}[\text{NiS}_4\text{C}_4\text{H}_4]$ (Interrante, Bray, Hart, Kasper, Piacente & Watkins, 1977), and cation stacks with different interplanar separations in $(\text{TTF})_2[\text{NiS}_4\text{C}_4\text{H}_4]$ (Kasper, Interrante & Secaur, 1975) and in $(\text{TMPD})_2[\text{Ni}(\text{mnt})_2]$, $\text{TMPD} = N,N,N',N'$ -tetramethyl-*p*-phenylenediamine (Hove, Hoffman & Ibers, 1972). The metal complexes do not stack in these cases, and electrical transport is due to the donor only.

N-Methylphenazine (NMP) forms segregated stacks in the charge-transfer complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Fritchie, 1966), which are highly conducting (Epstein, Conwell, Sandman & Miller, 1977; Fujii, Shirota & Nagano, 1977). Recent investigations reveal that structure and transport properties of systems based on NMP may be influenced by donor impurities such as phenazine and *N*-hydro-*N'*-methylphenazine (HMP) (Keller, Nöthe, Moroni & Soos, 1978; Morosin, 1978; Sandman, 1978). The properties of mixed phenazine/NMP-TCNQ systems have been investigated by Miller & Epstein (1978).

These observations prompted us to investigate the properties of compounds containing $[\text{NMP}]^+$ cations and bis(1,2-dithiolato)metal complexes. Here we report the preparation and structure of the 2:1 charge-transfer salt $[\text{NMP}]_2[\text{Ni}(\text{mnt})_2]$. Earlier papers dealt with the structures and properties of salts of the organic acceptor TCNQ and planar or nearly planar Pt complexes (Endres, Keller, Moroni, Nöthe & Vu Dong, 1978*a,b*; Vu Dong, Endres, Keller, Moroni & Nöthe, 1977).

Experimental

$\text{Na}_2(\text{mnt})$ was obtained according to Bähr & Schleitzer (1957). $[\text{NMP}]_2[\text{Ni}(\text{mnt})_2]$ was prepared in a similar way as described for other cations (Billig, Williams, Bernal, Waters & Gray, 1964; Weiher, Melby & Benson, 1964): 1.86 g (10 mmol) $\text{Na}_2(\text{mnt})$ and 3.07 g (10 mmol) $\text{NMP}^+\text{CH}_3\text{SO}_4^-$ were dissolved in 1:1 aqueous methanol and warmed. With stirring, a solution of 1.2 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 ml aqueous methanol was added in small portions. After cooling, the brown-orange precipitate was filtered off, washed with small portions of aqueous methanol, and dried in the air. 730 mg (1 mmol) of the powdery product were dissolved in a warm mixture of 20 ml ethanol, 20 ml acetonitrile, and 10 ml dimethyl sulfoxide. The solution was allowed to cool to room temperature and was kept overnight in a refrigerator. The resulting black needles were collected by filtration. Analysis: per cent found (calc.) C 54.52 (55.96), H 3.36 (3.02), N 15.19 (15.36), S 17.42 (17.50). A crystal with approximate dimensions $0.2 \times 0.1 \times 0.08$ mm was mounted with epoxy glue on top of a glass capillary. Orientation matrix and lattice constants (given in the *Abstract*) were calculated from the setting angles of 15 reflexions,

centered on a computer-controlled single-crystal diffractometer (Syntex $P2_1$, Mo $K\alpha$ radiation, graphite monochromator). Data collection (θ - 2θ scans, background-peak-background step scan mode, $5^\circ < 2\theta < 45^\circ$) yielded 1147 observed reflections with $I > 3.0\sigma(I)$. They were corrected with Lorentz, polarization and absorption factors, and statistical weights were assigned. Calculations were carried out with programs of the Enraf-Nonius *Structure Determination Package* on a PDP11/45 computer (Dept. of Chemistry, Stanford University). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974), and anomalous terms included. Plots were performed with the PDP11/45-Versatec plotter adaption of Johnson's (1965) *ORTEP*.

Structure determination and refinement

The systematic extinctions $h0l$, $h + l$ odd, and $0k0$, k odd determine space group $P2_1/n$ uniquely. A Patterson synthesis revealed the positions of Ni and S; the other nonhydrogen atoms could be located after two subsequent Fourier syntheses. The structure was refined with isotropic temperature factors to $R = 0.087$. All the parameters were further refined with anisotropic temperature factors for Ni and S. Finally, refinement with all the temperature factors anisotropic resulted in $R = 0.055$ (weighted $R = 0.065$). A difference Fourier synthesis showed as strongest peaks the positions of the H atoms. They were included in the calculations with fixed temperature factors $B = 4 \text{ \AA}^2$. With only the scale factor refined, R dropped to 0.054. Three reflections were rejected, which had structure factors just above the statistical threshold, and much lower calculated ones. R then became 0.053. Refinement of all the free parameters, based on 1144 reflections and including both $-h00$ and $+h00$, finally yielded after seven cycles $R = 0.041$ (weighted $R = 0.046$, max. shift/e.s.d. = 0.56).*

Description of the structure

The numbering scheme, bond distances and angles in the anion and cation are shown in Figs. 1 and 2. The bond lengths to H range from 0.88 (6) to 1.03 (6) Å. Atomic coordinates are listed in Table 1. Ni occupies inversion centers at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, so that the NiS_4 core is strictly planar. The maximum deviation of an atom of the $[\text{Ni}(\text{mnt})_2]^{2-}$ anion from a least-squares plane is 0.08 Å. The $[\text{NMP}]^+$ cation is very slightly

* Lists of structure factors, anisotropic thermal parameters, and deviations of atoms from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33988 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bent along the line N–N: least-squares planes through each half of the cation are tilted by 4° , with respect to each other, the maximum deviations from each plane being 0.02 and 0.01 Å, respectively. If a mean plane is calculated, the maximum deviation is 0.07 Å. Each anion is sandwiched between two cations, the dihedral angle between the mean plane through $[\text{NMP}]^+$ and the plane through $[\text{Ni}(\text{mnt})_2]^{2-}$ being 2.1° . The mean distance between the atoms of the cation and the plane through the anion is 3.48 Å. Fig. 3 shows the mode of overlap of $[\text{NMP}]^+$ and $[\text{Ni}(\text{mnt})_2]^{2-}$. A projection parallel to the molecular planes (Fig. 4) reveals that the $[\text{NMP}]_2[\text{Ni}(\text{mnt})_2]$ sandwiches form stacks along *a*. The interplanar distance between adjacent $[\text{NMP}]^+$ cations is 3.35 Å; the mode of overlap is presented in Fig. 5. A projection of the structure onto the *xz* plane is shown in Fig. 6.

Discussion

The title compound forms a kind of 'mixed stack' in the terminology of structures of charge-transfer complexes (Soos & Keller, 1977). The donor–acceptor sequence is *DAD–DAD*, with a pronounced overlap within a *DAD* unit and a very weak one between adjacent units. The compressed pellet conductivity of $6 \times 10^{-3} \Omega^{-1} \text{m}^{-1}$ shows that the carrier mobility along the stack is low.

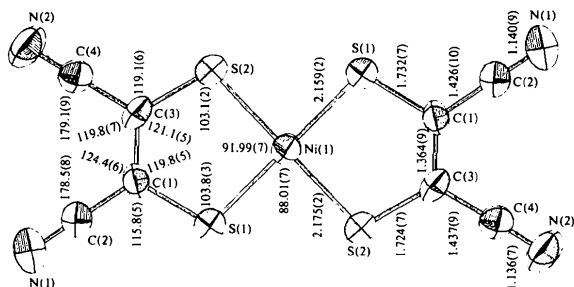


Fig. 1. The $[\text{Ni}(\text{mnt})_2]^{2-}$ anion with numbering scheme, bond lengths (Å) and angles ($^\circ$). Thermal ellipsoids are at 50%.

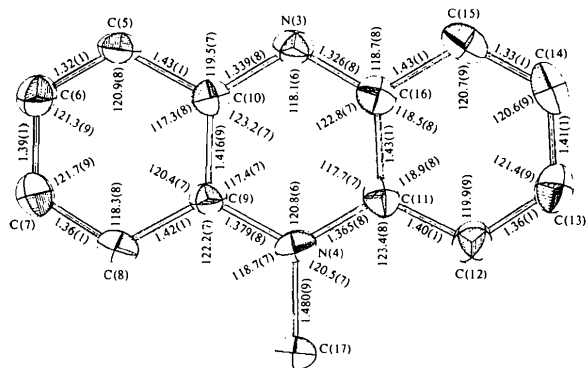


Fig. 2. The $[\text{NMP}]^+$ cation with numbering scheme, bond lengths (Å) and angles ($^\circ$). Thermal ellipsoids are at 30%.

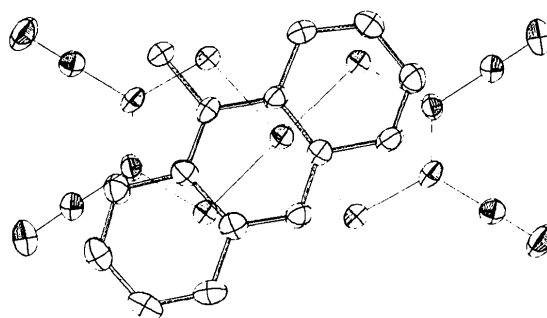


Fig. 3. Perpendicular projection of an $[\text{NMP}]^+$ onto the $[\text{Ni}(\text{mnt})_2]^{2-}$ of the same triad. 30% ellipsoids.

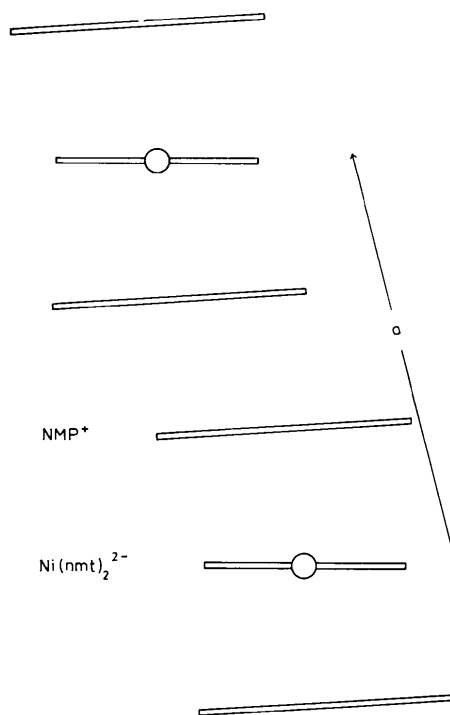


Fig. 4. Projection of a stack parallel to the plane through $[\text{Ni}(\text{mnt})_2]^{2-}$.

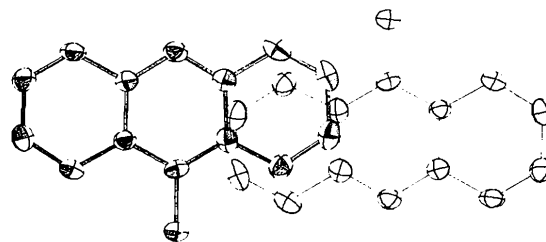
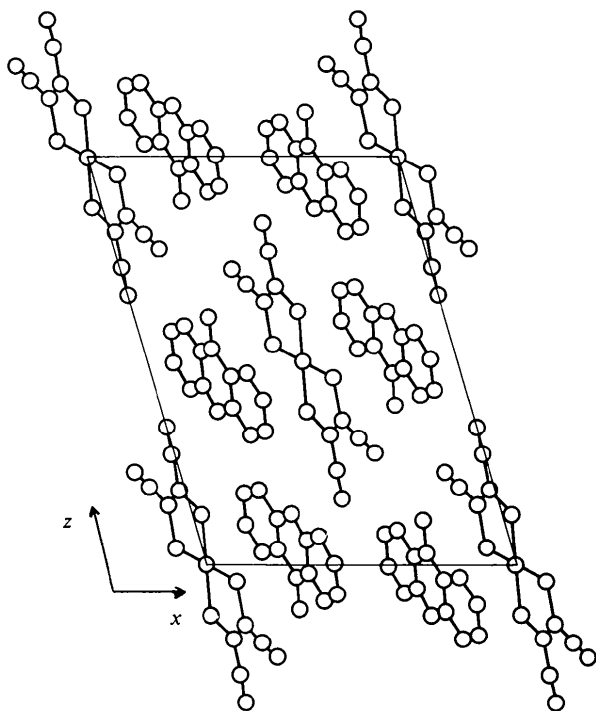


Fig. 5. Perpendicular projection of two $[\text{NMP}]^+$ of adjacent triads. 30% ellipsoids.

Fig. 6. Projection of the unit cell onto the *ac* plane.

Such a clustering to give sandwich-like units has not been observed before in charge-transfer complexes of bis(1,2-dithiolato)metal complexes. The structural types encountered hitherto are summarized in the introduction.

The bond distances in the $[\text{Ni}(\text{mnt})_2]^{2-}$ anion compare well with those quoted by Kobayashi & Sasaki (1977), and the Ni–S bond lengths differ clearly from those reported for the uninegative species. The cation is evidently $[\text{NMP}]^+$ and not $[\text{HMP}]^+$: no H atom bound to N(3) could be found in the difference Fourier map, which clearly revealed all the other H positions. The bond distances N(3)–C(10) [1.339 (8) Å] and N(3)–C(16) [1.326 (8) Å] correspond well with those reported for $[\text{NMP}]_2[\text{TCNQ}]_3$ (Sanz & Daly, 1975), 1.333 (7) and 1.336 (8) Å, and to the corresponding ones in *N*-ethylphenazinium TCNQ (Morosin, Plastas, Coleman & Stewart, 1978), 1.337 (4) and 1.332 (5) Å. They are in the range of those of the completely aromatic phenazine in α -phenazine TCNQ (Goldberg & Shmueli, 1973*b*), 1.338 (5) and 1.349 (4) Å. The corresponding distances in $[\text{HMP}]^+$ are clearly longer (Morosin, 1978), 1.355 (8) and 1.366 (8) Å in $[\text{HMP}][\text{ClO}_4]$, and 1.363 (5) and 1.382 (5) Å in $[\text{HMP}][\text{TCNQ}]$. The C–N bond lengths on the methyl side of the $[\text{NMP}]^+$ cation [1.365 (8) and 1.379 (8) Å] compare well with those found in the NMP and *N*-ethylphenazinium systems quoted above. They are slightly shorter than those in the less aromatic $[\text{HMP}]^+$ [1.386 (8) and

Table 1. Atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Ni(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)
S(1)	–0.0819 (2)	0.1971 (2)	0.0401 (1)
S(2)	0.0329 (2)	–0.1088 (2)	0.1234 (1)
N(1)	–0.1430 (5)	0.3752 (8)	0.2247 (4)
N(2)	0.0005 (5)	–0.0310 (7)	0.3379 (3)
N(3)	0.3186 (4)	0.0419 (6)	0.1258 (3)
N(4)	0.2781 (4)	0.1959 (7)	–0.0280 (3)
C(1)	–0.0671 (5)	0.1611 (8)	0.1460 (4)
C(2)	–0.1100 (6)	0.2788 (8)	0.1901 (4)
C(3)	–0.0179 (5)	0.0262 (7)	0.1815 (3)
C(4)	–0.0073 (5)	–0.0046 (8)	0.2690 (4)
C(5)	0.2380 (6)	0.2546 (8)	0.1832 (4)
C(6)	0.1857 (7)	0.3910 (9)	0.1735 (4)
C(7)	0.1629 (7)	0.4706 (8)	0.0977 (5)
C(8)	0.1930 (6)	0.4125 (8)	0.0300 (4)
C(9)	0.2468 (5)	0.2651 (8)	0.0378 (4)
C(10)	0.2701 (5)	0.1827 (8)	0.1149 (4)
C(11)	0.3218 (5)	0.0490 (7)	–0.0204 (4)
C(12)	0.3506 (5)	–0.0295 (9)	–0.0860 (4)
C(13)	0.3946 (6)	–0.1759 (9)	–0.0732 (5)
C(14)	0.4144 (6)	–0.2494 (8)	0.0056 (5)
C(15)	0.3882 (6)	–0.1787 (9)	0.0694 (5)
C(16)	0.3421 (5)	–0.0251 (8)	0.0600 (4)
C(17)	0.2585 (6)	0.2814 (9)	–0.1085 (4)
H(1)	0.257 (4)	0.184 (6)	0.229 (3)
H(2)	0.166 (4)	0.427 (6)	0.217 (3)
H(3)	0.124 (4)	0.564 (6)	0.090 (3)
H(4)	0.172 (4)	0.463 (6)	–0.018 (3)
H(5)	0.337 (4)	0.021 (6)	–0.136 (3)
H(6)	0.417 (4)	–0.223 (6)	–0.123 (3)
H(7)	0.441 (4)	–0.355 (6)	0.013 (3)
H(8)	0.403 (4)	–0.226 (6)	0.123 (3)
H(9)	0.288 (4)	0.220 (6)	–0.142 (3)
H(10)	0.181 (4)	0.316 (6)	–0.140 (3)
H(11)	0.295 (4)	0.388 (6)	–0.088 (3)

1.380 (8) Å] in $[\text{HMP}][\text{ClO}_4]$ and in $[\text{HMP}][\text{TCNQ}]$ [1.388 (5) and 1.386 (5) Å]. The corresponding distances in the dimethyl analog are 1.383 (4) and 1.389 (4) Å (Goldberg & Shmueli, 1973*a*).

This work was supported by Fonds der Chemischen Industrie and by Deutsche Forschungsgemeinschaft, especially through a travel grant to HE. The structure determination was carried out during a stay with the group of Professor W. A. Little, Stanford University, supported in part by the National Science Foundation (Grant No. DMR 76-82087-A02) and Office of Naval Research (Contract No. N0014-77-C-0631). The authors are indebted to Professor K. O. Hodgson, Dept. of Chemistry, Stanford University, for making available the diffractometer and computer facilities, which were procured in part through funds made available by the National Science Foundation Instrument Grant Program.

References

- ALCACER, L. & MAKI, A. H. (1974). *J. Phys. Chem.* **78**, 215–217.
 BÄHR, G. & SCHLEITZER, G. (1957). *Chem. Ber.* **90**, 438–443.

- BILLIG, E., WILLIAMS, R., BERNAL, I., WATERS, J. H. & GRAY, H. B. (1964). *Inorg. Chem.* **3**, 663–666.
- BRAY, J. W., HART, H. R. JR, INTERRANTE, L. V., JACOBS, I. S., KASPER, J. S., WATKINS, G. D., WEE, S. H. & BONNER, J. C. (1975). *Phys. Rev. Lett.* **35**, 744–747.
- EISENBERG, R. (1970). *Prog. Inorg. Chem.* **12**, 295–391.
- ENDRES, H., KELLER, H. J., MORONI, W., NÖTHE, D. & VU DONG (1978a). *Acta Cryst.* **B34**, 1703–1705.
- ENDRES, H., KELLER, H. J., MORONI, W., NÖTHE, D. & VU DONG (1978b). *Acta Cryst.* **B34**, 1823–1827.
- EPSTEIN, A. J., CONWELL, E. M., SANDMAN, D. J. & MILLER, J. S. (1977). *Solid State Commun.* **23**, 355–358.
- FORRESTER, J. D., ZALKIN, A. & TEMPLETON, D. H. (1964). *Inorg. Chem.* **3**, 1507–1515.
- FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 892–898.
- FUJII, G., SHIROTANI, I. & NAGANO, H. (1977). *Bull. Chem. Soc. Jpn*, **50**, 1726–1730.
- GOLDBERG, I. & SHMUELI, U. (1973a). *Acta Cryst.* **B29**, 421–431.
- GOLDBERG, I. & SHMUELI, U. (1973b). *Acta Cryst.* **B29**, 1440–1446.
- HÖVE, M. J., HOFFMAN, B. M. & IBERS, J. A. (1972). *J. Chem. Phys.* **56**, 3490–3502.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Birmingham: Kynoch Press.
- INTERRANTE, L. V., BRAY, J. W., HART, H. R. JR, KASPER, J. S., PIACENTE, P. A. & WATKINS, G. D. (1977). *J. Am. Chem. Soc.* **99**, 3523–3524.
- INTERRANTE, L. V., BROWALL, K. W., HART, H. R. JR, JACOBS, I. S., WATKINS, G. D. & WEE, S. H. (1975). *J. Am. Chem. Soc.* **97**, 889–890.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KASPER, I. S., INTERRANTE, L. V. & SECAUR, C. A. (1975). *J. Am. Chem. Soc.* **97**, 890–891.
- KELLER, H. J. (1977). Editor. *Chemistry and Physics of One-Dimensional Metals*. NATO ASI Series 25. New York & London: Plenum.
- KELLER, H. J., NÖTHE, D., MORONI, W. & SOOS, Z. G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 331–332.
- KOBAYASHI, A. & SASAKI, Y. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2650–2656.
- MCCLEVERTY, J. A. (1968). *Prog. Inorg. Chem.* **10**, 49–221.
- MILLER, J. S. (1978). Editor. *Synthesis and Properties of Low-Dimensional Materials*. *Ann. NY Acad. Sci.* **313**.
- MILLER, J. S. & EPSTEIN, A. J. (1978). *J. Am. Chem. Soc.* **100**, 1639–1641.
- MOROSIN, B. (1978). *Acta Cryst.* **B34**, 1905–1909.
- MOROSIN, B., PLASTAS, H., COLEMAN, L. B. & STEWART, J. M. (1978). *Acta Cryst.* **B34**, 540–543.
- PEREZ-ALBUERNE, N. A., ISETT, L. C. & HALLER, R. K. (1977). *J. Chem. Soc. Chem. Commun.* pp. 417–418.
- SANDMAN, D. J. (1978). *J. Am. Chem. Soc.* **100**, 5230–5232.
- SANZ, F. & DALY, J. J. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 1146–1150.
- SCHMITT, R. D., WING, R. M. & MAKI, A. H. (1969). *J. Am. Chem. Soc.* **91**, 4394–4401.
- SOOS, Z. G. & KELLER, H. J. (1977). In *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. KELLER, pp. 391–412. NATO ASI Series 25. New York & London: Plenum.
- VU DONG, ENDRES, H., KELLER, H. J., MORONI, W. & NÖTHE, D. (1977). *Acta Cryst.* **B33**, 2428–2431.
- WEIHER, J. F., MELBY, L. R. & BENSON, R. E. (1964). *J. Am. Chem. Soc.* **86**, 4329–4333.
- WHELAND, R. C. & GILSON, J. L. (1976). *J. Am. Chem. Soc.* **98**, 3916–3925.
- WUDL, F. (1975). *J. Am. Chem. Soc.* **97**, 1962–1963.
- WUDL, F., HO, C. H. & NAGEL, A. (1973). *J. Chem. Soc. Chem. Commun.* p. 923.

Acta Cryst. (1979). **B35**, 357–360

The Crystal and Molecular Structure of the Cuprous–Cupric Complex Aquabis(ethylenediamine)copper(II) Dicyanodi(selenocyanato)cuprate(I)

BY V. VRABEL AND J. GARAJ

Department of Analytical Chemistry, Slovak Technical University, Janska 1, 880 37 Bratislava, Czechoslovakia

AND L. KUTSCHABSKY

Zentralinstitut für physikalische Chemie, DAW, 1199 Berlin, Adlershof, Rudower Chaussee 5, German Democratic Republic

(Received 17 July 1978; accepted 11 October 1978)

Abstract

$[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_2(\text{SeCN})_2]$, $\text{C}_8\text{H}_{18}\text{Cu}_3\text{N}_8\text{OSe}_2$ is monoclinic, space group *Cc*, with $a = 8.879$ (2), $b = 15.824$ (1), $c = 13.493$ (2) Å, $\beta = 106.80$ (1)°, $Z = 4$. The structure was refined to $R = 0.069$ for 1381 counter reflections. The crystal struc-

ture is formed of cations $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ and polymeric anions $[\text{Cu}_2(\text{CN})_2(\text{SeCN})_2]^{2-}$. The coordination about the Cu^{II} atom is square-pyramidal with two molecules of ethylenediamine and one molecule of water at the apex. The Cu^{I} atoms are tetrahedrally bonded by SeCN and CN, these being present as bridges.