BISDISELENOLATE METAL COMPLEXES. SYNTHESIS, STRUCTURE AND ELECTROCHEMICAL PROPERTIES

Sheng-Gao Liu[a]; Yun-Qi Liu[a]; Xue-Yong Yang[a]; Dao-Ben Zhu[a]

[a] Institute of Chemistry, Academia Sinica, Beijing, Peoples Republic of China

PLEASE SCROLL DOWN FOR ARTICLE

BISDISELENOLATE METAL COMPLEXES. SYNTHESIS, STRUCTURE AND ELECTROCHEMICAL PROPERTIES

SHENG-GAO LIU, YUN-QI LIU, XUE-YONG YANG and DAO-BEN ZHU

*Institute of Chemistry, Academia Sinica,
Beijing 100080, Peoples Republic of China*

The multi-selenium donor ligand 2,2-dicyanoethylene-1,1-diselenolate (DCNSe) has been prepared. The dianionic complex of DCNSe with Ni(II) has been isolated as the tetrabutylammonium (TBA) salt. The compound is characterized by negative ion Fast Atom Bombardment (FAB) mass spectral analysis, Fourier Transform Infrared (FT-IR) spectral analysis, UV-Vis spectral analysis and cyclic voltammetry. The electrochemical properties and crystal structure are studied as well. In addition, the corresponding Cu(II) complex has been isolated as the TBA salt and characterized by negative ion FAB mass spectral analysis and FT-IR spectral analysis.

Key words: Multi-selenium donor ligand, transition metal complex, crystal structure, electrochemical properties, synthetic metals.

INTRODUCTION

Since the discovery of the first "SYNTHETIC METAL" TTF-TCNQ (tetrathiafulvalene-tetracyano-*p*-quinodimethane),[1] there has been widespread interest in the experimental properties and theoretical models for these materials. There is a wealth of carefully determined experimental data on these organic conductors and superconductors and a number of theories have been proposed to rationalize and explain the properties of these materials. Dozens of new donors, mostly of a heterocyclic nature and containing chalcogen atoms, as well as a number of new acceptors have been synthesized and co-crystallized in order to tune and improve the conductivity, transition temperature and also to get superconducting states. So far, more than 40 molecular superconductors have been prepared and characterized.[2] At least, six different families of molecular superconductors can be considered in addition to the fullerene (C_{60}) family. Five of these can be derived from the TMTSF (tetramethyl-tetraselenafulvalene), BEDT-TTF [bis-(ethylenedithio)-tetrathiafulvalene], DMET (4,5-dimethyl-4'5'-ethylenedithio-1,3-diselena-1',3'-dithiafulvalene), MDT-TTF (4,5-methylenedithiotetrathiafulvalene), and BEDO-TTF [bis(ethylenedioxy)-tetrathiafulvalene] organic donors, respectively, and the sixth one from transition metal complexes of multi-sulfur donor ligand DMIT (1,3-dithiol-2-thione-4,5-dithiolate). During the last decade, there has been growing interest in the transition metal complexes of multi-sulfur donor ligands because they are promising candidates for constituents of molecular conductors or superconductors. These acceptor complexes are of particular interest due to the many

TABLE I

Molecular superconductors derived from metal bisdithiolene complexes and
their Tc values

No.	Compound	Tc(K)	Year	Ref.
1	(TTF)[Ni(dmit)$_2$]$_2$	1.62(7 Kbar)	1986	5
2	(Me$_4$N)[Ni(dmit)$_2$]$_2$	5.0 (7 Kbar)	1987	6
3	α'-(TTF)[Pd(dmit)$_2$]$_2$	5.93(24 Kbar)	1989	7
4	α-(TTF)[Pd(dmit)$_2$]$_2$	1.7(22 Kbar)	1990	7
5	β-(Me$_4$N)[Pd(dmit)$_2$]$_2$	6.2(6.5 Kbar)	1991	8
6	(Me$_2$Et$_2$N)[Ni(dmit)$_2$]$_2$	4.0(2.4 Kbar)	1992	9
7	α-(EDT-TTF)[Ni(dmit)$_2$]$_2$	1.3*	1993	10

* ambient pressure.

possibilities for chemical modifications such as changes in the chelating metal, and/
or in the ligand itself, and/or in the countercation or donor molecule in the derived
non-integer oxidation state or charge transfer compounds. Up to now, a large
variety of conducting compounds based on [M(DMIT)$_2$]$^{n-}$ have been synthesized
by varying the countercations and the chelating metals.[3] Among these compounds,
the seven superconducting states that have been found are listed in Table I.[4]

It has been suggested that high polarizability, a delocalized electronic state, low
on-site coulomb energy and effective interchain interactions are required for a
complex to be a good conductor and superconductor. As part of an exploration of
new potential candidates for conductive complexes, we have earlier reported the
synthesis, structure and electrical properties of a series of charge transfer (CT)
compounds derived from bis(2,2-dicyanoethylene-1,1-dithiolato) transition metal
complexes, i.e. [M(DCNT)$_2$]$^-$.[11] The fairly high conductivity of the M(DCNT)$_2$-
based CT complexes encouraged us to explore another possible chemical modifi-
cation, the exchange of the sulfur atoms with selenium atoms.[11,12] Through these
substitutions, the selenium isolog of the DCNT ligand, DCNSe (2,2-dicyanoethyl-
ene-1,1-diselenolate), (CN)$_2$C=CSe$_2^{2-}$, was prepared.

It is more convenient to use selenium analogues in the study of low-dimensional
synthetic metals in order to obtain complexes with more effective and stronger
interchain interactions. The reason for this is that the selenium atom has more
spatially extended and diffuse orbitals than the sulfur atom (van der Waals radius
of S: 1.80, Se: 1.90[13]). In addition, using selenium analogues will increase the
conduction band width and polarizability and hence, an enhancement of metallic
character may be expected.

In this communication, we report the synthesis, characterization, structure and
electrochemical properties of bis(tetrabutylammonium)-bis(2,2-dicyanoethylene-1,1-
diselenolato) nickelate(II) and the synthesis and characterization of the corre-
sponding Cu(II) complex.

EXPERIMENTAL

Preparation of 2,2-dicyanoethylene-1,1-diselenolato dipotassium salt, **1**:   To a 1 M ethanolic potassium
hydroxide solution was added 1.98 g (0.03 mol) of malononitrile and 5.2 g (0.03 mol) of CSe$_2$. After
stirring for 40 min at $-5°C$ under Ar, the resulting solution was poured into 1500 mL of ether. After

staying in a refrigerator for 2 hrs, the solids were separated by filtration, washed with ether (3 × 5 mL) and dried under vacuum. Yield 5.92 g (64.8%) of crystalline powder.

Preparation of Bis(tetrabutylammonium)-bis(2,2-dicyanoethylene-1,1-diselenolato) nickelate(II), $(TBA)_2Ni(DCNSe)_2$, 2: To an aqueous solution of 1 (0.63 g, 2 mmol) was added 10 mL aqueous solution containing $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol). After stirring for 20 min at 50°C under Ar and filtering, a hot aqueous solution of TBABr (0.65 g, 2 mmol) was added to the filtrate in order to precipitate the products. The crude products were collected by filtration, washed twice with methanol (2 × 5 mL) and dried in air. Recrystallization from a solution of acetone/methanol (2:1), gave 0.68 g of brown crystals (67.1%). M.p. 200–202°C. Negative ion FAB showed m/e (intensity): 530 (M^{2-}, 40). Anal. calc. for $C_{40}H_{72}N_6Se_4Ni$: C 47.49; H 7.17; N 8.31%; found C 47.48; H 7.18; N 8.28%. FT-IR (KBr, cm^{-1}): 2961 (ν_{C-H}, s), 2874 (ν_{C-H}, m), 2205 ($\nu_{C\equiv N}$, s), 2197 ($\nu_{C\equiv N}$, s), 1483 ($\nu_{C=C}$, m-w), 1464 (δ_{C-H}, m-w), 1412 (δ_{C-H}, s), 1368 (δ_{C-H}, s), 848 (ν_{C-Se}, m), 738 (ν_{C-Se}, m).

Preparation of Bis(tetrabutylammonium)-bis(2,2-dicyanoethylene-1,1-diselenolato) cuprate (II), $(TBA)_2Cu(DCNSe)_2$: The complex was prepared in the same manner as above. M.p. 199–200°C. Negative ion FAB showed m/e (intensity): 535 (M^{2-}, 12). Anal. calc. for $C_{40}H_{72}N_6Se_4Cu$: C 47.22; H 7.08; N 8.26%; found C 47.50; H 7.28; N 8.35%. FT-IR (KBr, cm^{-1}): 2964 (ν_{C-H}, s), 2878 (ν_{C-H}, m), 2195 ($\nu_{C\equiv N}$, s), 2179 ($\nu_{C\equiv N}$, s), 1470 ($\nu_{C=C}$, m-w), 1402 (δ_{C-H}, m), 847 (ν_{C-Se}, w), 740 (ν_{C-Se}, w).

Elemental analyses were performed by the Analysis & Measurement Center of our institute with a Carlo Erba 1106 apparatus.

Infrared spectra were recorded on a Bruker IFS-113V Fourier Transform Infrared spectrophotometer in the region of 4000–400 cm^{-1} with KBr pellets at room temperature.

UV-Vis spectra were recorded by a HITACHI 340 spectrophotometer in ethanol solution.

Cyclic voltammetric measurements were performed with a EG&G PARC MODEL 175 UNIVERSAL PROGRAMMER and a MODEL 174A POLAROGRAPHIC ANALYZER at room temperature using DMF solutions containing the $[TBA]_2[Ni(DCNSe)_2]$ complex (2 mM) and a supporting electrolyte of $TBABF_4$ (0.1 M). A platinum disc (3 mm in diameter) was used as a working electrode. The counter electrode was a platinum plate which was immersed directly in the electrolyte solution. A saturated calomel electrode (SCE) was used as reference electrode and also directly immersed in the electrolyte. The solution was deaerated by bubbling with nitrogen gas before measurements. Scan rate was 20 mV/s.
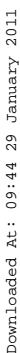
X-Ray Data Collection and Structure Determination

Intensity measurements were collected on a RASA-IIS RIGAKU four-circle diffractometer with ω-2θ scans. Structure solution and refinements were performed using direct methods and conventional least-squares and Fourier techniques.[14,15]

Deposit supplementary material concerned with the X-ray crystallographic work with the Cambridge Crystallographic Data Centre, UK.

RESULTS AND DISCUSSION

The synthetic procedure is summarized in Scheme I. The negative ion FAB mass spectra of $[TBA]_2[Ni(DCNSe)_2]$ and $[TBA]_2[Cu(DCNSe)_2]$ are similar. Both anions in the complex salts were present in the mass spectra with many isotopic peaks. But the fragmentation patterns differ in important details. The anion part of the Ni complex was observed along with fragments with m/z of 450 (M^{2-}-Se, 21%) and 374 (M^{2-}-Se-C_4N_2, 20%) and several smaller fragments. In the case of the Cu complex, the anion part was observed along with a fragment with m/z of 455 (M^{2-}-Se, 6%) and several smaller fragments which were hard to assign.
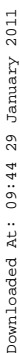
The IR spectra of $[TBA]_2[Ni(DCNSe)_2]$ and $[TBA]_2[Cu(DCNSe)_2]$ are similar and are dominated by strong, sharp $\nu_{C\equiv N}$ bands at 2200 ± 5 and 2187 ± 10 cm^{-1}, respectively. But for the Ni complex, the peaks of the $\nu_{C\equiv N}$ bands are found at a *higher frequency* by about 10 and 20 cm^{-1}, respectively, than the corresponding

SCHEME I

ones in the Cu complex. Another great difference appears in the $\nu_{C=C}$ and δ_{C-H} (δs or δas) region. In the case of the Ni complex, there are four strong or medium peaks in this region and the $\nu_{C=C}$ band is observed at 1483 cm^{-1} with a medium-weak peak. In contrast, in the case of the Cu complex, there are only two broad peaks centered at 1470 (m) and 1402 (s) cm^{-1}, respectively.

The UV-Vis spectrum of the Ni complex is shown in Figure 1. One of our reasons for the study of the UV-Vis spectrum comes from the π-electron delocalization in the ligand which may be vital for the solid state properties of the metal complexes

FIGURE 1   UV-Vis spectrum of [TBA]$_2$[Ni(DCNSe)$_2$] in ethanol solution.

containing it. The spectrum of the complex shows the characteristic bands of the conjugated C=C and C≡N groups at 224.1 and 296.0, 314.3 nm, respectively. The π-electron delocalization absorption band over the two ligands through the central metal ion and the four selenide bridges lies at 367.3 nm. This could be important evidence for an interaction of d-orbitals of the central metal ion with the π-orbitals on the two ethylene double bonds through the orbitals on Se and then further interacting with the other π-orbitals on the four C≡N bonds through the conjugated system in the ligand. This is similar to that observed in the Ni-DMID complexes.[16]

Figure 2 presents the cyclic voltammogram of $[TBA]_2[Ni(DCNSe)_2]$. It shows two irreversible oxidation peaks around 0.3 V and 0.67 V, respectively, and a redissolution peak R at -0.35 V. Unlike most other $[ML_2]^{n-}$ (n = 1, 2; L = multi-sulfur or multi-selenium ligands) complexes, this complex does not show any reversible redox reactions between -1.0 and 0.9 V. The voltammogram shows a sharp increase in the intensity of the anodic peak followed by a smooth decrease, and a rather high intensity of the redissolution peak R. These features are characteristic of a modification of the electrode, and are usually explained by assuming deposition of a conducting species on the electrode during the oxidation process.[17] Under stationary conditions and with the increase of scan cycles, a black layer covering the surface of the electrode is observed. The redissolution peak intensity
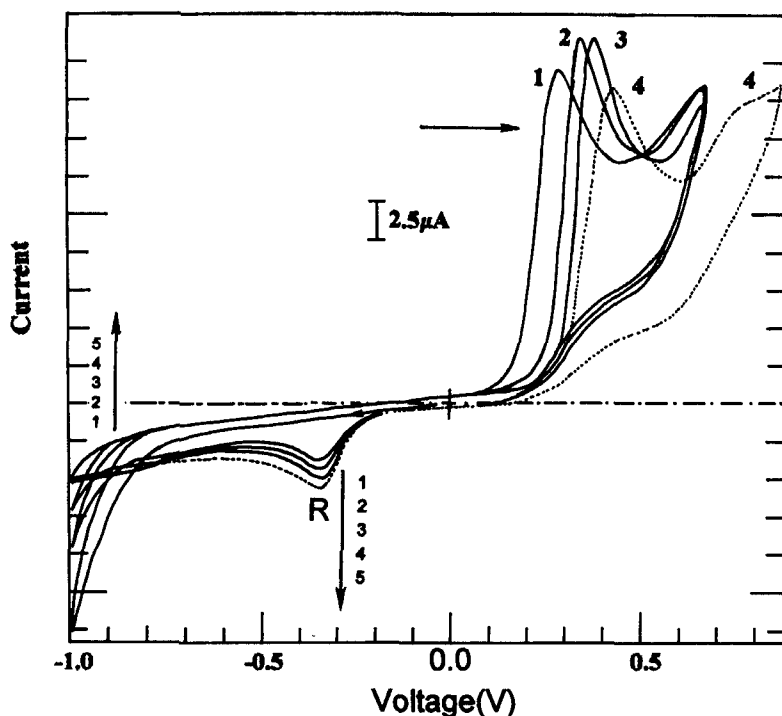
FIGURE 2   Cyclic voltammogram of $[TBA]_2[Ni(DCNSe)_2]$ between -1.0 V and 0.7 V (solid curves 1–3) or 0.9 V (dashed, curve 4) (2 mM in DMF, 0.1 M TBABF$_4$, 3 mm diameter Pt disc working electrode, vs SCE, 20 mV/s).

seems related to the amounts of materials deposited on the electrode: with the increase of scan cycles, the first oxidation peak goes to more anodic potentials; from 0.29 V for the first cycle to 0.35 V for the second and to 0.39 V for the third. When the oxidation peak is going to more anodic potentials, an increase in the current of the redissolution peak R is observed (Figure 2), indicating that the black deposit is electrically conductive. This deposit is probably made of the non-integer oxidation state species.[18]

To study whether or not the metal complexes may be good conducting materials, they have to be either oxidized into non-integer ones or complexed with organic donors such as BEDT-TTF, TTF, to form charge transfer compounds by either chemical or electrochemical methods. Studies on all these aspects are now undertaken by us.

Figure 3 shows the crystal structure of the Ni complex. The compound crystallizes in the triclinic, space group $P\bar{1}$ with a $= 11.306(9)$ Å, b $= 12.749(7)$ Å, c $= 9.656(8)$ Å, $\alpha = 91.58(9)°$, $\beta = 118.53(9)°$, $\gamma = 93.79(8)°$, V $= 1217.35$ Å^3, Dc $= 1.379$
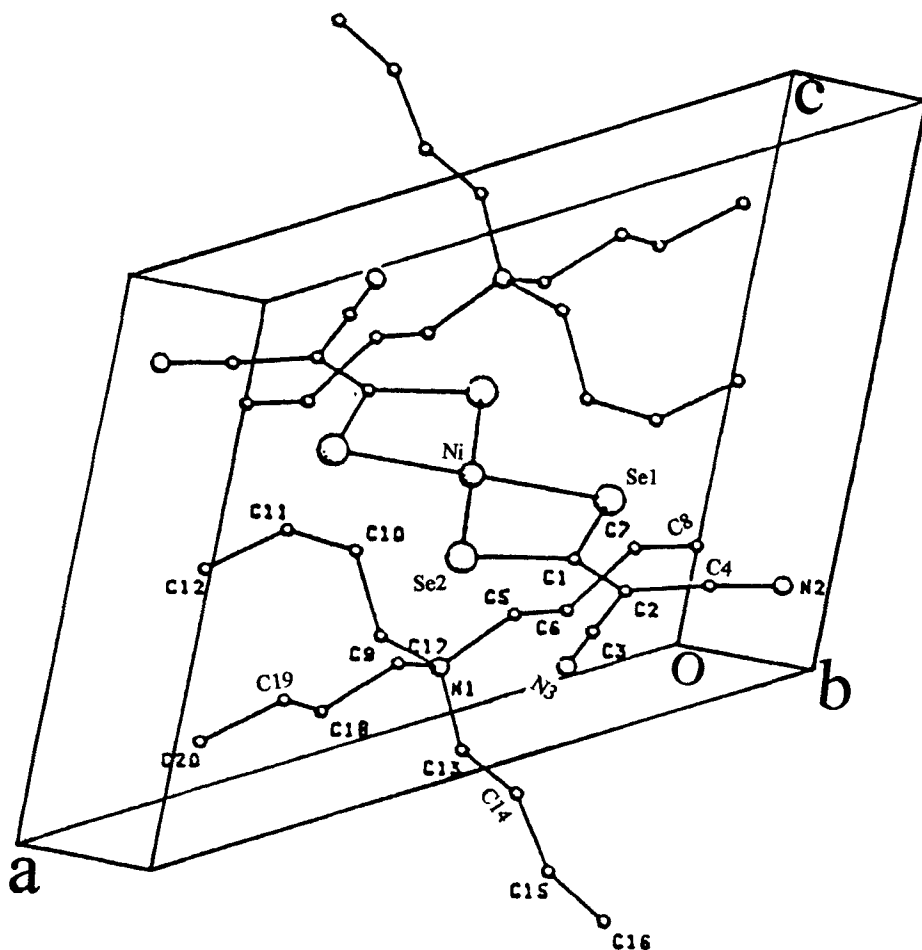

FIGURE 3 Crystal structure of [TBA]$_2$[Ni(DCNSe)$_2$] with atom numbering.

$g \cdot cm^3$, and $Z = 1$. Table II presents the atomic parameters. Table III presents the bond distances and angles. In the cations, the N atoms are sp^3 hybridized, each bonded to four butyl groups in a tetrahedral configuration. The C—N—C angles lie between 106.2(10) and 111.9(10)° and are thus close to 109.5° reported for a tetrahedron. The N—C bond distances vary from 1.509(15) to 1.544(16) Å, slightly longer than that of the common N—C bond lengths (1.47 Å). In addition, the atoms in the $[N(C_4H_9)_4]^+$ cation show considerable thermal motion and the standard deviations of the positions and the bond lengths are therefore high (see Tables II and III). The C—C distances have values between 1.496(22) and 1.590(19) Å. In $[TBA]_2[Ni(dmit)_2]$, the C—C distances in the cation have values between 1.52(2) and 1.58(2) Å.[19]

In the anion, the central Ni(II) atom is dsp^2 hybridized and forms a squareplanar configuration with the four Se atoms. The Ni—Se(1) bond distance (2.316 Å) is almost equal to that of Ni-Se(2) (2.319 Å) and very close to the sum of the covalent radii of Ni and Se atoms (2.31 Å). The C(1), C(2), C(3), C(4), N(2), and N(3) atoms are nearly coplanar forming a least-squares plane with a mean deviation of 0.02 Å. The C(4) atom is deviating most from the plane with a distance of 0.04 Å.

TABLE II

Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) with e.s.d.'s in parentheses in the asymmetric unit

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

Atom	X	Y	Z	$Ueq \times 10^{-2}$
Ni	0.5	0.5	0.5	6.0(1)
Se1	0.2777(2)	0.5414(2)	0.3787(2)	7.2(1)
Se2	0.5215(2)	0.6440(1)	0.3696(2)	6.8(1)
C1	0.3407(12)	0.6570(10)	0.3021(13)	5.7(3)
C2	0.2651(11)	0.7332(10)	0.2222(12)	5.0(3)
C3	0.3224(12)	0.8239(10)	0.1728(13)	6.1(3)
C4	0.1314(13)	0.7354(11)	0.1848(14)	7.5(3)
C5	0.3250(11)	0.2396(10)	0.1787(13)	5.8(3)
C6	0.2216(12)	0.1406(10)	0.1450(13)	6.0(3)
C7	0.1392(12)	0.1757(11)	0.2277(14)	6.9(3)
C8	0.0219(13)	0.0890(12)	0.1862(14)	8.1(3)
C9	0.5121(12)	0.1338(10)	0.2011(13)	5.8(3)
C10	0.5834(12)	0.1473(11)	0.3801(14)	6.8(3)
C11	0.6800(13)	0.0540(11)	0.4471(14)	7.1(3)
C12	0.8023(13)	0.0719(12)	0.4220(15)	8.4(3)
C13	0.3563(12)	0.1939(10)	-0.0547(13)	5.8(3)
C14	0.2718(11)	0.2760(10)	-0.1588(13)	5.5(3)
C15	0.1837(12)	0.2239(11)	-0.3289(14)	6.6(3)
C16	0.0996(13)	0.3105(11)	-0.4398(14)	7.4(3)
C17	0.5174(11)	0.3279(10)	0.1637(13)	5.4(3)
C18	0.6265(12)	0.3253(11)	0.1182(14)	6.6(3)
C19	0.7141(13)	0.4342(12)	0.1744(14)	7.8(3)
C20	0.8354(13)	0.4368(12)	0.1427(14)	7.6(3)
N1	0.4265(10)	0.2234(8)	0.1206(11)	5.7(3)
N2	0.0154(13)	0.7340(11)	0.1431(14)	10.6(3)
N3	0.3862(11)	0.8814(10)	0.1314(13)	7.7(3)

S.-G. LIU *et al.*

TABLE III
Selected bond lengths and angles in [TBA]$_2$[Ni(DCNSe)$_2$]

Bond lengths(Å)

Ni-Se1	2.316(2)	Ni-Se2	2.319(2)	Se1-C1	1.911(14)
Se2-C1	1.847(13)	C1-C2	1.338(17)	C2-C3	1.394(20)
C2-C4	1.378(19)	C3-N3	1.151(20)	C4-N2	1.173(20)
N1-C5	1.522(20)	C5-C6	1.526(18)	C6-C7	1.546(23)
C7-C8	1.554(20)	N1-C9	1.524(16)	C9-C10	1.517(16)
N1-C13	1.509(15)	C13-C14	1.514(16)	C14-C15	1.556(15)
C15-C16	1.581(18)	N1-C17	1.544(16)	C17-C18	1.496(22)
C18-C19	1.571(19)	C19-C20	1.539(24)	C10-C11	1.590(19)
C11-C12	1.518(24)				

Bond angles(°)

Se2-Ni-Se1	81.1(1)	C1-Se1-Ni	85.4(4)
C1-Se2-Ni	86.8(4)	Se2-C1-Se1	106.6(6)
C2-C1-Se1	124.4(11)	C2-C1-Se2	129.0(11)
C3-C2-C1	119.2(12)	C4-C2-C1	122.8(13)
C4-C2-C3	118.1(11)	N3-C3-C2	179.0(15)
N2-C4-C2	175.5(15)	N1-C5-C6	115.4(11)
C7-C6-C5	106.4(11)	C8-C7-C6	109.9(11)
N1-C9-C10	113.7(11)	C11-C10-C9	107.9(11)
C12-C11-C10	110.9(12)	N1-C13-C14	115.5(11)
C15-C14-C13	108.2(10)	C16-C15-C14	108.4(10)
N1-C17-C18	113.5(11)	C19-C18-C17	108.2(12)
C20-C19-C18	112.1(13)	C17-N1-C13	111.9(10)
C17-N1-C5	106.2(10)	C17-N1-C9	109.9(8)
C13-N1-C5	111.3(9)	C13-N1-C9	106.6(10)
C9-N1-C5	111.0(11)		

The dihedral angle between the least-squares plane and the anion plane is 5.69°. The bond distances of C(1)—C(2) (1.338 Å), C(2)—C(3) (1.394 Å), and C(2)—C(4) (1.378 Å) lie between the C—C single bond length (1.54 Å) and C=C double bond length (1.337 Å). This indicates that all these carbon atoms are strongly conjugated.

Due to the bulky cations, the anions are perfectly isolated from each other. No significant interanionic contacts, normally responsible for the formation of a conducting band, exists, and therefore the electrical conductivity of the salt must be very low showing that it is an insulator.

REFERENCES

1. J. Ferraris, D. O. Cowan, V. V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
2. E. B. Yagubskii, *Mol. Cryst. Liq. Cryst.*, **230**, 139 (1993).

3. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).
4. S. G. Liu, M.S. Thesis, pp. 14 (1994).
5. L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica B & C (Amsterdam)*, **143**, 378 (1986).
6. A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1819 (1987).
7. L. Brossard, M. Ribault, L. Valade and P. Cassoux, *J. Phys. (Paris)*, **50**, 1521 (1989).
8. K. Kajita, Y. Nishio, S. Moriyama, R. Kato, H. Kobayashi, W. Sasaki, A. Kobayashi, H. Kim and Y. Sasaki, *Solid State Comm.*, **65**, 361 (1988).
9. (a) A. Kobayashi, H. Kim, Y. Sasaki, K. Murata, R. Kato and H. Kobayashi, *J. Chem. Soc. Faraday Trans.*, **86**, 361 (1990); (b) A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R. A. Clark and A. E. Underhill, *Chem. Lett.*, 2163 (1991).
10. H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Sato, H. Kobayashi and H. Kuroda, *Chem. Lett.*, 1235 (1993).
11. D. B. Zhu, X. C. Xing, P. J. Wu, P. Wang, D. M. Zhang and D. L. Yang, *Synth. Met.*, **41–43**, 2541 (1991).
12. K. A. Jensen, *Quarterly Reports on Sulfur Chemistry*, **5**, 45 (1970).
13. (a) G. Saito, T. Enoki and H. Inokuchi, *Chem. Lett.*, 503 (1983) and two references therein reported: (1) P. M. Chaikin, P. Haen, E. M. Englen and R. L. Greene, *Phys. Rev.*, *B*, **24**, 7155 (1981); (2) F. Wudl, *J. Am. Chem. Soc.*, **103**, 7064 (1981); (b) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1976).
14. S. G. Liu, N. C. Shi, P. J. Wu and D. B. Zhu, *Acta Cryst. (C)*, in press (1995).
15. S. G. Liu, P. J. Wu, X. Y. Yang and D. B. Zhu, *Mol. Cryst. Liq. Cryst.*, in press (1995).
16. S. G. Liu, P. J. Wu, Y. F. Li and D. B. Zhu, *Phosphorus, Sulfur, and Silicon*, **90**, 219 (1994).
17. J. P. Cornelissen, J. G. Haasnoot, J. Reedijk, C. Faulmann, J.-P. Legros, P. Cassoux and P. J. Nigrey, *Inorg. Chim. Acta*, **202**, 131 (1992) and two references therein reported: (a) L. Valade, M. Bousseau and P. Cassoux, *Nouv. J. Chim.*, **9**, 351 (1985); (b) L. Valade, P. Cassoux, A. Gleizes and L. V. Interrante, *J. Phys. (Paris), Colloq.*, **44**, C3, 1183 (1983).
18. J. B. Tommasino, B. Pomarede, D. Medus, D. de Montauzon, P. Cassoux and P.-L. Fabre, *Mol. Cryst. Liq. Cryst.*, paper galley (1993).
19. O. Lindqvist, L. Sjölin, J. Sieler, G. Steimecke and E. Hoyer, *Acta Chem. Scand., A*, **33**, 445 (1979).