atoms of the organic molecule and iodine or chlorine atoms of the same or adjacent chains.

Extensive use of the Cambridge Crystallographic Data Files has been made for the bibliographic search.

References

BIGOLI, F., LEPORATI, E. & PELLINGHELLI, M. A. (1978). *Cryst. Struct. Commun.* 7, 527–530.

CANNAS, M., MARONGIU, G. & SABA, G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2090–2094.

CRAMER, R. E., MAYNARD, R. B. & IBERS, J. A. (1981). *J. Am. Chem. Soc.* 103, 76–81.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–100, 149–150. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

SHELDRICK, G. M. (1976). *SHELX76.* A program for crystal structure determination. Univ. of Cambridge, England.

Structure of Trimethyl(phenyl)ammonium Bis[dimercaptomaleodinitrilato(2—)-S,S']nickelate(III), [N(CH₃)₃(C₆H₅)][Ni(C₄N₂S₂)₂]

BY C. MAHADEVAN, M. SESHASAYEE AND B. V. R. MURTHY

Department of Physics, Indian Institute of Technology, Madras 600 036, India

AND P. KUPPUSAMY AND P. T. MANOHARAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Abstract. $M_r = 475.28$, monoclinic, $P2_1/n$, $a = 14.737$ (1), $b = 7.296$ (9), $c = 20.970$ (3) Å, $\beta = 108.931$ (8)°, $V = 2133$ Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.237$ mm⁻¹, $F(000) = 960$, room temperature, final $R = 0.056$ for 1860 unique reflections. The stacking of the anion is diadic and one-dimensional along the *b* axis.

Introduction. The 1,2-dithiolato ligands $R_2C_2S_2^{2-}$ are known to form transition-metal complexes having remarkable oxidation–reduction behaviour, including the formation of abnormal valence states of the metal (McCleverty, 1968; Wing & Schlupp, 1970). These metal chelates often crystallize with columnar ionic packing arrangements in the solid state, which produces interesting magnetic, electrical and optical properties. Some of the d^7 chelates with Ni, Pd and Pt have been found to exhibit an antiferromagnetic exchange along the chain (Maki, Edelstein, Davison & Holm, 1964). Magnetic studies together with X-ray data suggest that the spin correlation occurs through S-atom *d*-orbital interaction with the metal ion of an adjacent chelate molecule (Weiher, Melby & Benson, 1964). Such pairwise spin correlation is very sensitive to the intrastack separation, which in turn depends on the nature and bulkiness of the cation used. For example, in the case of R^+.Ni(mnt)$_2^-$ [mnt: dimercaptomaleodinitrilato(2—)] where R^+ is spherical quaternary ammonium (Kobayashi & Sasaki, 1977) or phosphonium

(Fritchie, 1966), or a planar cation like tropylium (Manoharan, Noordik, de Boer & Keijzers, 1981), *N*-methylphenazinium (Kuppusamy, Mahadevan, Seshasayee & Manoharan, 1983), or *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Ramakrishna & Manoharan, 1983 *a*) segregated stacking of cations and chelate anions has been observed. Of these, systems with an alternating chelate stack (dimeric) are found to have strong exchange demagnetization ($J \sim 400$–600 cm⁻¹) (Weiher, Melby & Benson, 1964). Recent EPR work on [NEt₄] [Ni(mnt)₂] showed the system to be distinctive in being by far the best example of a one-dimensional (1D) system (Ramakrishna & Manoharan, 1983 *b*).

We are studying the magnetic behaviour (by EPR and susceptibility measurements) to obtain a clear understanding of the cooperative phenomenon existing in such low-dimensional systems. In this paper we report the crystal and molecular structure of the title compound {[NMe₃Ph][Ni(mnt)₂] hereafter}.

Experimental. Black, shiny needles of [NMe₃Ph] [Ni(mnt)₂] obtained by the procedure of Davison & Holm (1967) using trimethyl(phenyl)ammonium iodide as the quaternary ammonium salt.

Unit-cell parameters obtained by least-squares refinement of the θ values of 25 high-angle reflections. Crystal 0.35 × 0.13 × 0.65 mm, three-dimensional intensity data collected on an Enraf–Nonius CAD-4

diffractometer with graphite-monochromated Mo $K\alpha$ radiation. $\omega/2\theta$ scan mode. Standard reflections ($5\bar{1}\bar{1}$ and $\bar{5}0\bar{1}$) showed no significant change. All reflections (h: -17 to 17, k: 0 to 8, l: 0 to 25) in the range $2° < 2\theta < 52°$ were measured. Maximum counting time for each reflection 60 s. 1860 unique reflections with $I > 3\sigma(I)$ considered observed. R_{int} from merging 59 equivalent reflections 0·035. The systematic absences ($h0l$ with $h+l$ odd, $0k0$ with k odd) fix the space group unambiguously as $P2_1/n$. Intensities not corrected for absorption.

Structure solved by heavy-atom method and refined by full-matrix least squares with SHELX76 (Sheldrick, 1976). Initially the atoms were assigned individual isotropic thermal parameters and refinement of 109 positional and thermal parameters including the scale factor converged to $R = 0·106$. Large thermal parameters ranging from 0·06 Å^2 (for Ni) to 0·18 Å^2 [for C(15)] were found, with large values for C(15), C(16), C(17) and the anionic N atoms. Finally, the atoms were allowed to vibrate anisotropically and refinement of 244 positional and thermal parameters including the scale factor converged to $R = 0·056$. Maximum and average shift/e.s.d 0·456 and 0·012 respectively. Atomic scattering factors for Ni^{3+} from Cromer (1965) and for other non-hydrogen atoms from Cromer & Mann (1968); anomalous-dispersion correction factors from Cromer & Liberman (1970). Final

difference Fourier maps featureless and did not reveal the positions of H atoms. Maximum height in final difference Fourier map 0·53 e Å^{-3}. $\sum w|\Delta F|^2$ minimized. $R_w = 0·074$ with $w = 0·027/[\sigma^2(F_o) + 0·150|F_o|^2]$.

Discussion. The fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Table 2 contains the relevant bond lengths and bond angles.* An ORTEP plot (Johnson, 1965) of the molecule is shown in Fig. 1.

The Ni atom has an approximate square-planar configuration with all four Ni–S distances equal within experimental error. The average Ni–S bond distance [2·142 (2) Å] compares well with those of similar monoanionic structures: [PMePh₃][Ni(mnt)₂], compound (I) (Fritchie, 1966) [2·146 (1) Å]; [C₇H₇][Ni{S₂C₂(CF₃)₂}₂] (Wing & Schlupp, 1970) [2·135 (4) Å]; [NEt₄][Ni(mnt)₂], compound (II)

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^4$ *for* Ni *and* $\times 10^3$ *for others*) *with estimated standard deviations in parentheses*

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ni	5637 (1)	2273 (2)	5308 (1)	674 (8)
S(1)	5803 (2)	1676 (4)	4350 (1)	70 (2)
S(2)	7082 (2)	1499 (5)	5849 (2)	82 (2)
S(3)	4168 (2)	2916 (4)	4776 (1)	70 (2)
S(4)	5508 (2)	2989 (5)	6266 (1)	84 (2)
C(1)	6967 (8)	950 (13)	4578 (6)	73 (4)
C(2)	7531 (8)	831 (14)	5210 (6)	73 (5)
C(3)	3732 (8)	3583 (13)	5414 (5)	70 (4)
C(4)	4333 (8)	3598 (14)	6063 (6)	76 (4)
C(5)	7308 (9)	437 (16)	4029 (7)	93 (5)
C(6)	8522 (9)	226 (17)	5417 (7)	95 (5)
C(7)	2753 (10)	4120 (15)	5235 (6)	83 (5)
C(8)	3989 (9)	4206 (16)	6598 (7)	94 (5)
N(1)	7584 (9)	16 (17)	3607 (7)	139 (5)
N(2)	9284 (9)	−242 (19)	5597 (7)	144 (5)
N(3)	1995 (8)	4571 (16)	5117 (6)	117 (5)
N(4)	3726 (9)	4693 (17)	7020 (6)	137 (5)
C(9)	1819 (10)	5225 (23)	2670 (7)	116 (5)
C(10)	1766 (10)	4020 (21)	3137 (7)	122 (5)
C(11)	983 (10)	3992 (20)	3381 (6)	110 (5)
C(12)	274 (8)	5269 (16)	3132 (5)	74 (5)
C(13)	290 (9)	6562 (20)	2638 (6)	106 (5)
C(14)	1094 (11)	6503 (22)	2425 (7)	121 (5)
N(5)	−559 (6)	5258 (12)	3401 (5)	78 (4)
C(15)	−222 (11)	5706 (36)	4106 (8)	264 (5)
C(16)	−1241 (12)	6765 (27)	3128 (10)	207 (5)
C(17)	−1068 (14)	3561 (22)	3259 (13)	244 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Cation

C(9)–C(10)	1·34 (2)	C(10)–C(11)	1·41 (2)
C(11)–C(12)	1·37 (2)	C(12)–C(13)	1·41 (2)
C(13)–C(14)	1·40 (2)	C(9)–C(14)	1·39 (2)
C(12)–N(5)	1·51 (2)	N(5)–C(15)	1·44 (2)
N(5)–C(16)	1·47 (2)	N(5)–C(17)	1·43 (2)
C(14)–C(9)–C(10)	120 (1)	C(9)–C(10)–C(11)	122 (1)
C(10)–C(11)–C(12)	118 (1)	C(11)–C(12)–C(13)	123 (1)
C(12)–C(13)–C(14)	116 (1)	C(13)–C(14)–C(9)	122 (1)
C(11)–C(12)–N(5)	118 (1)	C(13)–C(12)–N(5)	119 (1)
C(12)–N(5)–C(15)	109 (1)	C(12)–N(5)–C(16)	113 (1)
C(12)–N(5)–C(17)	111 (1)	C(15)–N(5)–C(16)	101 (1)
C(15)–N(5)–C(17)	113 (1)	C(16)–N(5)–C(17)	109 (1)

Anion

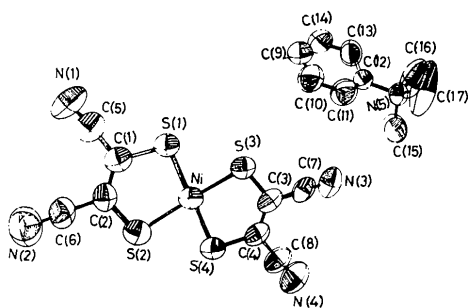|			
Ni–S(1)	2·146 (3)	Ni–S(2)	2·138 (3)
Ni–S(3)	2·142 (3)	Ni–S(4)	2·143 (3)
S(1)–C(1)	1·71 (1)	S(2)–C(2)	1·75 (1)
S(3)–C(3)	1·73 (1)	S(4)–C(4)	1·70 (1)
C(1)–C(2)	1·32 (2)	C(3)–C(4)	1·36 (1)
C(1)–C(5)	1·45 (2)	C(2)–C(6)	1·45 (2)
C(3)–C(7)	1·42 (2)	C(4)–C(8)	1·44 (2)
C(5)–N(1)	1·13 (2)	C(6)–N(2)	1·12 (2)
C(7)–N(3)	1·11 (2)	C(8)–N(4)	1·13 (2)
S(1)–Ni–S(2)	92·7 (2)	S(1)–Ni–S(3)	87·7 (2)
S(2)–Ni–S(4)	86·7 (2)	S(3)–Ni–S(4)	93·0 (2)
S(1)–Ni–S(4)	177·3 (2)	S(2)–Ni–S(3)	177·2 (2)
C(1)–S(1)–Ni	102·1 (5)	C(2)–S(2)–Ni	103·1 (5)
C(3)–S(3)–Ni	103·0 (4)	C(4)–S(4)–Ni	102·9 (5)
S(1)–C(1)–C(2)	123·4 (9)	S(2)–C(2)–C(1)	118·7 (9)
S(3)–C(3)–C(4)	119·4 (9)	S(4)–C(4)–C(3)	121·8 (9)
S(1)–C(1)–C(5)	115·7 (9)	S(2)–C(2)–C(6)	116·8 (9)
S(3)–C(3)–C(7)	118·1 (9)	S(4)–C(4)–C(8)	118·2 (9)
C(5)–C(1)–C(2)	121 (1)	C(6)–C(2)–C(1)	125 (1)
C(7)–C(3)–C(4)	123 (1)	C(8)–C(4)–C(3)	120 (1)
C(1)–C(5)–N(1)	179 (2)	C(2)–C(6)–N(2)	178 (2)
C(3)–C(7)–N(3)	177 (2)	C(4)–C(8)–N(4)	179 (2)

Fig. 1. Perspective view of the molecule.

(Kobayashi & Sasaki, 1977) (2·149 Å); $[C_7H_7][Ni(mnt)_2]$, compound (III) (Manoharan, Noordik, de Boer & Keijzers, 1981) [2·145 (1) Å]; $[C_{10}H_{16}N_2][Ni(mnt)_2]$, compound (IV) (Ramakrishna & Manoharan, 1983a) [2·152 (4) Å]; $[C_{13}H_{11}N_2][Ni(mnt)_2]$, compound (V) (Kuppusamy, Mahadevan, Seshasayee & Manoharan, 1983) [2·138 (1) Å]; and $[N(n-Bu)_4][Ni\{S_2C_2(C_6H_5)_2\}_2]$ (Mahadevan, Seshasayee, Kuppusamy & Manoharan, 1983) [2·137 (3) Å]. The Ni atom is displaced out of the basal plane of the S atoms by only 0·001 Å.

The intraligand S—S distances are 3·099 (4) [S(1)—S(2)] and 3·109 (3) Å [S(3)—S(4)]. The interligand S—S distances are 2·971 (4) [S(1)—S(3)] and 2·940 (5) Å [S(2)—S(4)]. These distances compare well with those of similar compounds having square-planar geometry. Also, the interligand S—S value is relatively shorter than the van der Waals distance and is taken as an indication of inter-donor-atom bonding forces which help stabilize the square-planar coordination.

The four C—S distances vary from 1·70 (1) to 1·75 (1) Å, the variation being statistically insignificant according to the χ^2 distribution test. The mean is 1·72 (1) Å which is considerably shorter than the sum of covalent radii (1·81 Å). If the hybridization state of the C atom approaches sp^2, the C_{sp^2}—S_{sp^3} length would be 1·77 Å and if that of the S atom also approaches sp^2, the C_{sp^2}—S_{sp^2} length would be perhaps 1·74—1·73 Å giving rise to a Ni—S distance of 2·20 Å. Since the observed Ni—S and S—C distances are shorter than these proposed standards, some multiple bonding involving the S atom is doubtless present. Comparable values for the C—S lengths are found in monoanionic compounds with Ni as the metal atom: compound (I) [1·714 (4)]; compound(II) (1·720); compound (III) (1·719); compound (IV) [1·708 (15)]; and compound (V) [1·710 (4) Å]. The dianionic compounds, with the same mnt ligand and Ni as the metal atom, have larger mean S—C distances ranging from 1·728 to 1·750 Å.

The C_{sp^2}—C_{sp^2} single-bond lengths vary from 1·42 (2) to 1·45 (2) Å. The mean distance [1·44 (1) Å] compares well with those of similar compounds (monoanionic as well as dianionic): compound (I) [1·430 (5)];

compound (II) (1·440); compound (III) (1·432); compound (IV) [1·431 (18)]; compound (V) [1·433 (3)]; $[NMe_4][Ni(mnt)_2]$ (Eisenberg & Ibers, 1965) (1·410); $[N(n-Bu)_4]_2[Ni(mnt_2)]$ (Kobayashi & Sasaki, 1977) (1·432); $[C_{10}H_{16}N_2]_2[Ni(mnt)_2]$ (Hove, Hoffman & Ibers, 1972) [1·420 (10)]; and $[C_{13}H_{11}N_2]_2[Ni(mnt)_2]$ (Endres, Keller, Moroni & Nöthe, 1979) (1·432 Å).

A statistical-significance test shows that the difference in the two C=C double-bond distances (0·04 Å) is only marginally significant. However, the significance of such a difference can be crucial to a detailed description of the bonding in this complex, and it may therefore be necessary to look to other physical methods which can provide the needed information. In the case of $V\{S_2C_2(C_6H_5)\}_3$ (Eisenberg & Gray, 1967), the discrepancy in the C=C double-bond distances is again marginally significant. However, the mean C=C distance of the present structure is nearly equal to the standard value (1·338 Å).

The bite angles [92·7 (2) and 93·0 (2)°] of the chelate rings are very nearly equal. The corresponding bond angles are nearly the same in both chelates and also compare well with those found in the mnt ligand in various compounds.

The calculated least-squares plane through all the atoms in the anion shows that the anion as a whole is planar to within 0·09 (1) Å. Deviations of individual atoms from the plane presumably result from packing distortions. Although statistically significant, these deviations are considerably smaller than the amplitudes of thermal motion. In conclusion, we can approximate the molecular symmetry to D_{2h}.

The $Ni(mnt)_2$ units stack in columns along the b axis in the order (i) x,y,z, (ii) $\bar{x},\bar{y},\bar{z}$, (iii) x, $1 + y$, z, (iv) $\bar{x}$, $1-y$, $\bar{z}$,...with Ni^i—Ni^{ii}, Ni^{ii}—Ni^{iii}, Ni^{iii}—Ni^{iv}, Ni^i—Ni^{iii} and Ni^{ii}—Ni^{iv} distances being 4·411 (5), 3·825 (4), 4·411 (5), 7·296 (9) and 7·296 (9) Å respectively. This shows that the metal atoms are not collinear along the stack axis but form a kind of kinked chain. The Ni—Ni contacts are shown separately in Fig. 2.

Since the Ni^{III} atom has a square-planar low-spin d-electron configuration, the isolated, i.e. magnetically dilute, anion is a ground-state doublet. This electron configuration is in agreement with molecular-orbital calculations (Eisenberg, Ibers, Clark & Gray, 1964) for the corresponding dianion. Thus, in the Ni^{III} chelate, the unpaired electron of an isolated anion is associated with the metal d_{xy} orbital.

The spin of the anion is antiferromagnetically coupled to that of the nearby anion which forms a pair with the first one with an Ni—Ni distance of 3·825 (4) Å by three steps, namely (1) delocalization to an in-plane-bonded S by $Ni_{d_{xy}}$—(empty $S_{d_{xy}}$) overlap [bond distance 2·142 (3) Å], (2) polarization by spin exchange of the weak Ni—S bond [3·531 (5) Å] that is formed by the interaction of the doubly occupied d_{z^2}
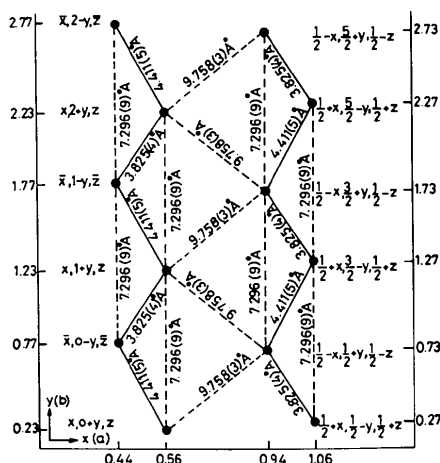
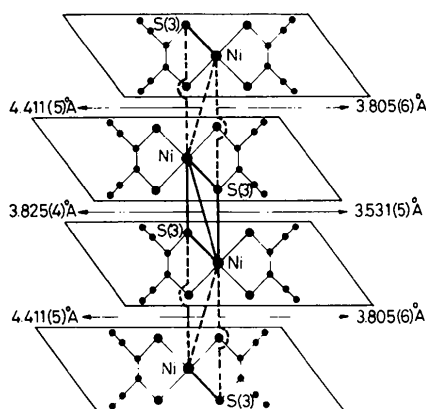Fig. 2. Schematic diagram showing the Ni–Ni contacts.

Fig. 3. Schematic diagram showing the Ni–S overlaps.

orbital of the second Ni atom with the empty $S_{d_z^2}$ orbital, and (3) correlation with the unpaired electron in the d_{xy} orbital of the second Ni atom by spin exchange. The strength of the antiferromagnetic coupling is enhanced by the cooperation of two correlation paths per pair.

The Ni–Ni contact and the secondary Ni–S distances between pairs along the column are 4·411 (5) and 3·805 (6) Å respectively. These distances are longer compared to those within the pair. This is shown schematically in Fig. 3. There are two magnetically inequivalent sites by virtue of orientation of the two normals to the chelate planes which subtend angles of ± 20° with the b axis.

The system may be somewhat stabilized by the partial back donation of the Ni d_{z^2} pair and the Ni d_{xy} electron to the S atom, thus compensating for the removal of charge from the S atom by the primary Ni–S bonding. On the basis of this, the strength of the antiferromagnetic interaction coupling the doublets into

singlet ground-state pairs should be quite sensitive to small changes in Ni nearest out-of-plane S distances.

A similar type of columnar packing has been found in compound (I) and compound (II). Other inter- and intramolecular anion–cation contacts are normal.

In looking for 1D materials, one will choose a system in which well defined exchange pathways exist in only one direction. These pathways sometimes involve one or more ligand atoms which are coordinated to two adjacent metal ions. Highly 1D systems can be obtained (a) by using larger counterions and bulky substituents in either the cationic or anionic part to separate the chains well from each other and also (b) by enhancing the isotropic exchange within the chain thus making the ratio of interchain interaction to intrachain interaction as small as possible.

In the present structure, the closest Ni–Ni contact occurs along the chains and the shortest interchain Ni–Ni distance is comparatively longer [9·758 (3) Å] (Fig. 2), thus making the system highly 1D. As we feel that this system will serve as a good candidate for studying low-dimensional exchange properties, we plan to carry out further investigations by making magnetic and electrical measurements.

References

CROMER, D. T. (1965). Acta Cryst. 18, 104–109.
CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.
DAVISON, A. & HOLM, R. H. (1967). Inorg. Synth. 10, 8–26.
EISENBERG, R. & GRAY, H. B. (1967). Inorg. Chem. 6, 1844–1849.
EISENBERG, R. & IBERS, J. A. (1965). Inorg. Chem. 4, 605–608.
EISENBERG, R., IBERS, J. A., CLARK, R. J. H. & GRAY, H. B. (1964). J. Am. Chem. Soc. 86, 113–115.
ENDRES, H., KELLER, H. J., MORONI, W. & NÖTHE, D. (1979). Acta Cryst. B35, 353–357.
FRITCHIE, C. J. JR (1966). Acta Cryst. 20, 107–118.
HOVE, M. J., HOFFMAN, B. M. & IBERS, J. A. (1972). J. Chem. Phys. 56, 3490–3502.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KOBAYASHI, A. & SASAKI, Y. (1977). Bull. Chem. Soc. Jpn, 50, 2650–2656.
KUPPUSAMY, P., MAHADEVAN, C., SESHASAYEE, M. & MANOHARAN, P. T. (1983). To be published.
MCCLEVERTY, J. A. (1968). Prog. Inorg. Chem. 10, 49–221.
MAHADEVAN, C., SESHASAYEE, M., KUPPUSAMY, P. & MANOHARAN, P. T. (1983). To be published.
MAKI, A. H., EDELSTEIN, N., DAVISON, A. & HOLM, R. H. (1964). J. Am. Chem. Soc. 86, 4580–4587.
MANOHARAN, P. T., NOORDIK, J. H., DE BOER, E. & KEIJZERS, C. P. (1981). J. Chem. Phys. 74, 1980–1989.
RAMAKRISHNA, B. L. & MANOHARAN, P. T. (1983a). Inorg. Chem. In the press.
RAMAKRISHNA, B. L. & MANOHARAN, P. T. (1983b). Inorg. Chem. In the press.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
WEIHER, J. F., MELBY, L. R. & BENSON, R. E. (1964) J. Am. Chem. Soc. 86, 4329–4333.
WING, R. M. & SCHLUPP, R. L. (1970). Inorg. Chem. 9, 471–475.