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Syntheses and Structure of Ni(III) Complexes with 1-Toluene-3,4-dithiole. Bond-Valence Approach to the Oxidation State of the Central Atom

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The complex compounds of the formula (R)[$\text{Ni}^{\text{III}}(\text{tdt})_2$], R = Met_4N (**I**), Et_4N (**II**), Pr_4N (**III**), MePh_3P (**IV**), Ph_4P (**V**); tdt = 1-toluene-3,4-dithiole have been synthesized. The crystal structures of the compounds **III** and **IV**were determined by X-rays studies. Bond valence as a function of inter-nuclear distance for Ni–S bonds was estimated. On the basis of physico-chemical measurements and bond-valence sum model, the formal oxidation state III of Ni atoms for both structures was proposed.

Key words: nickel(III)dithiolene complexes, crystal structure, synthesis, physico-chemical measurements, bond valences

Metal bis(1,2-dithiolene) complexes have been recently studied due to potential applications as superconductors [1], unusual magnetic properties [2] and optical non-linearities [3]. Moreover, dithiolates as ligands are able to stabilize the higher oxidation states of the central atom [4–6]. Bond-valence (BV) method [7–14] is based on the valence sum rule (1) [15,16]. Bond valence is a quantity (s) fulfilling (1) for all atoms of crystal structure:

$$V_i = \sum_j s_{ij} \tag{1}$$

V_i is the valence (formal charge or oxidation state) of atom i and s_{ij} is the valence of a bond between atoms i and j. The empirical expression [17–20] for the calculation of bond valences is

$$s_{ij} = \exp[(R_{ij} - r_{ij})/b] \tag{2}$$

where r_{ij} is internuclear distance. b is commonly adopted constant 0.37 Å [18] and R_{ij} is bond-valence parameter tabulated in [14]. Recently formulae (1) and (2) in metal organic compounds have been examined [21–26]. Focusing on the immediate vicinity of the metal atom BV method has been transformed into the bond-valence sum

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(BVS) model. Based on metal-ligand orbital interaction, the bond-valence dependence on the internuclear distance was developed [27] in the form (3):

$$s_{ij} = \frac{\alpha_1}{r_{ij}} + \frac{\alpha_2}{r_{ij}^2} + \frac{\alpha_3}{r_{ij}^3} + \frac{\alpha_4}{r_{ij}^4} + \frac{\alpha_5}{r_{ij}^5} \tag{3}$$

α_i are constants dependent on the types of bonded atoms.

This paper comprises syntheses of several nickel complexes with 1-toluene-3,4-dithiole as a ligand and their study by common physico-chemical methods, including X-ray structural analysis of two selected complexes containing cations $(Pr_4N)^+$ and $(MePh_3P)^+$. The results are discussed with those obtained from BVS calculations.

EXPERIMENTAL

Materials and methods: 1-Toluene-3,4-dithiole was manufactured by FLUKA Co, other reagents were from LACHEMA Co; all reagents used were of p.a. purity. The content of nickel was determined by chelatometric titration using murexide as an indicator. The elemental analyses (C, H, N, S) were performed on an EA 1108 device (FISONS INSTRUMENT, Italy). Diffuse-reflectance UV-VIS spectra (45000–11000 cm^{-1}) were measured on a Specord M 40 (CARL ZEISS, Jena) and IR spectra (400–300 cm^{-1}) on a Specord M 80 spectrophotometer (CARL ZEISS, Jena) in nujol. Magnetochemical measurements were carried out on a laboratory designed (Palacký University, Olomouc) instrument by Faraday method with $Co[Hg(SCN)_4]$ as a calibrant. Diamagnetic corrections were calculated with Pascal's constants [28]. The molar conductivity was estimated by the Conductivity Meter OK-102/1 (RADELKIS, Budapest) at 25°C in dimethylformamide ($c = 10^{-3}$ mol dm^{-3}).

Syntheses: All compounds were synthesized by the following general procedure. To metallic potassium (3.3 mmol) in methanol (20 cm^3) 1-toluene-3,4-dithiole (1.6 mmol) in methanol (10 cm^3) and later under stirring the methanolic solution of $NiCl_2{\cdot}6H_2O$ (10 cm^3) were dropwise added. The resulting red solution was stirred for two hours and methanolic solution of appropriate ammonium (phosphonium) salt (1.6 mmol) was added. The resulting green substance was filtered, washed by methanol and dried at 40°C under infra-lamp. The crystals suitable for X-ray analysis were obtained by recrystallization from acetone. Yields about 50%. Analyses in the limits of the experimental error led to the following formulae of the studied complexes; **I**. $(Met_4N)[Ni(tdt)_2]$, **II**. $(Et_4N)[Ni(tdt)_2]$, **III**. $(Pr_4N)[Ni(tdt)_2]$, **IV**. $(MePh_3P)[Ni(tdt)_2]$, **V**. $(Ph_4P)[Ni(tdt)_2]$.

X-ray crystallography: For two selected complexes, $(Pr_4N)[Ni(tdt)_2]$ (**III**) and $(MePh_3P)[Ni(tdt)_2]$ (**IV**), the X-ray structures were solved. The data were collected for **III** on CAD-4 diffractometer (ENRAF-NONIUS) with graphite monochromated CuK_α radiation, whereas in the case of **IV** the KUMA KM-4 diffractometer with MoK_α radiation was used. Both structures were solved by direct methods using the SHELXS-97 program [29] and refined anisotropically by the full-matrix least-squares procedure using SHELXL-97 program package [30]. For complex **IV** two molecules of water were found in the structure. Most of hydrogen atoms were found from Fourier maps and they were refined isotropically. In the case of **IV** the absorption correction according DIFABS [31] was applied. Additional calculations were made using PARST-95 program [32].

Bond-valence calculations: The parameters α_i in equation (3) for Ni–S bond were calculated *via* minimization of the function (4) by the procedure described in [27]:

$$Q = \sum_{k=1}^{n} (Z_k - V_k)^2 \tag{4}$$

n is the number of independent nickel atoms and Z_k is their formal oxidation states. For the calculations were used the structures stored in the Cambridge Structural Database [33] (CSD) and the Inorganic Crystal Structure Database (ICSD) [34]. The structure was accepted if around the central atom (Ni) within the sphere of radius 3.0 Å only the terminal atoms of the same type (S) were contained. Hydrogen atoms were not considered. The structures with value $R = \sum||F_o|-|F_c|| / \sum|F_o| > 0.06$ and the structures with the disordered atoms were excluded as well. The best agreement parameters were achieved if $\alpha_5 = 0$. The selected results of all calculations are shown in Table 1.

Table 1. Parameters of the Ni–S bond valence function.

α_1 [Å]	α_2 [Å^2]	α_3 [Å^3]	α_4 [Å^4]	n	D^a	Q_{min}
–27.80	85.08	53.19	–215.28	186	0.001	0.055

[a] r.m.s. relative deviation [9] $D = \sqrt{\sum_{k=1}^{n}(Z_k - V_k)^2 / Z_k^2 / n}$

RESULTS AND DISCUSSION

Results of physico-chemical studies are given in Table 2. Apparently, all compounds are paramagnetic at room temperature. The effective magnetic moments correspond to one unpaired electron. Moreover, for the compounds **III** and **IV** the temperature dependence of μ_{eff} was measured (see Figs. 1 and 2). The susceptibility is virtually independent of temperature and the Curie-Weiss model can be applied.

Table 2. The results of physico-chemical measurements.

	Complex	μ_{eff} [BM]	λ_M [Scm^{2}mol^{-1}]	UV/VIS [x10^{3}cm^{-1}]			IR ν(C-S) [cm^{-1}]
I.	$(Met_4N)[Ni(tdt)_2]$	2.42	65	19.2	27.2	32.2	812 s
II.	$(Et_4N)[Ni(tdt)_2]$	2.22	60	19.4	27.1	31.9	804 s
III.	$(Pr_4N)[Ni(tdt)_2]$	1.85	not measured	19.0	27.4	31.4	810 s
IV.	$(MePh_3P)[Ni(tdt)_2]$	1.87	71	19.4	25.0	31.6	814 m
V.	$(Ph_4P)[Ni(tdt)_2]$	1.86	67	19.2	26.5	31.2	820 m

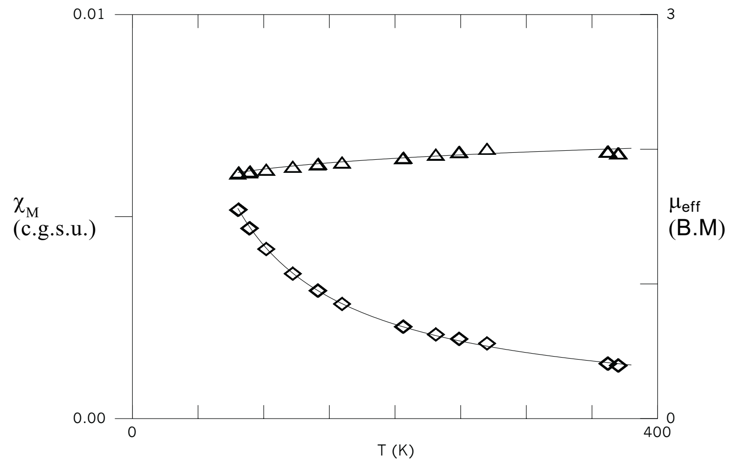

Figure 1. Dependence of magnetic susceptibility and effective magnetic moment on temperature for $(Pr_4N)[Ni(tdt)_2]$ (**III**).

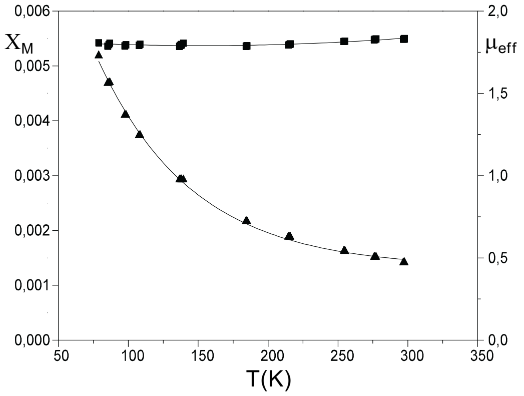

Figure 2. Dependence of magnetic susceptibility and effective magnetic moment on temperature for $(MePh_3P)[Ni(tdt)_2]\cdot 2H_2O$ (**IV**).

No exchange magnetic interaction between paramagnetic centers was found. These facts can be explained by assuming the presence of Ni(III) species. This possibility was recently discussed for similar complexes with NiS_4 chromophore [6]. Electronic and IR spectra for all compounds exhibit similar absorption maxima typical of square-planar coordination of nickel and valence vibration due to C–S bond in the dithiolate. The values of molar conductivity in the dimethylformamide solution are characteristic for 1:1 electrolyte [35], which is in good agreement with the conclusions above.

Crystal structures: For final confirmation of the square planar geometry of the coordination sphere around central atom the crystal structures for two complexes **III**, **IV** with different cations were solved. The basic crystallographic parameters including basic information about data collection are summarized in Table 3. Selected bond lengths and angles are in Table 4. Both structures contain the complex $[Ni(tdt)_2]^-$ ions and cations $(Pr_4N)^+$ (**III**), $(MePh_3P)^+$ (**IV**) (Figs. 3 and 4). The structure of **IV** contains two non-equivalent toluenedithiole ligands. The packing of the structure units in the unit cell of **IV** is shown in Fig. 5. The methyl groups from toluenedithiole ligands are disordered in two positions with occupation factors equal to 0.5 (see Fig. 5). The water molecules are mutually held by the hydrogen bonds (Table 5).

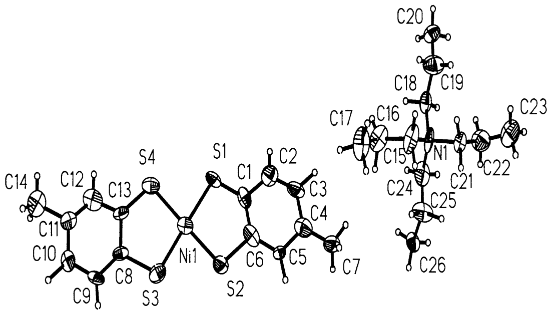

Figure 3. The molecular structure of $(Pr_4N)[Ni(tdt)_2]$ (**III**). 40% thermal ellipsoids are drawn for non-hydrogen atoms.

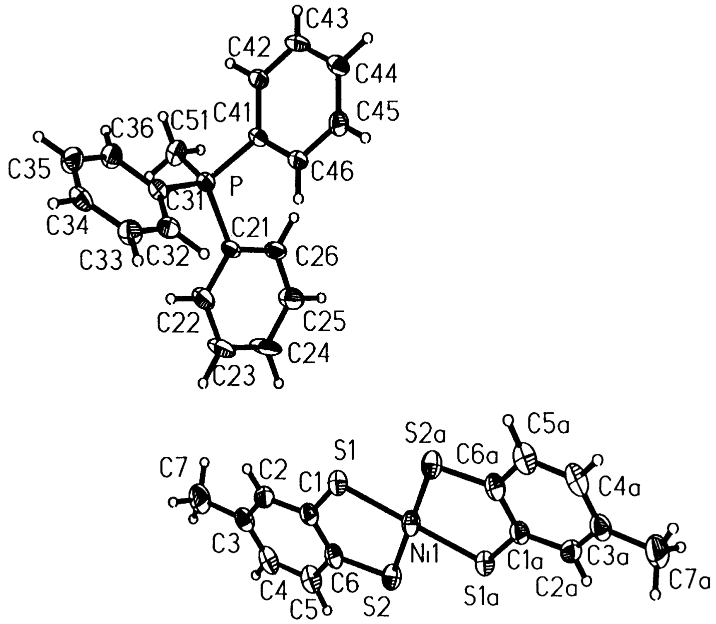

Figure 4. The molecular structure of (MePh$_3$P)[Ni(tdt)$_2$]·2H$_2$O (**IV**). 40% thermal ellipsoids are shown for non-hydrogen atoms.

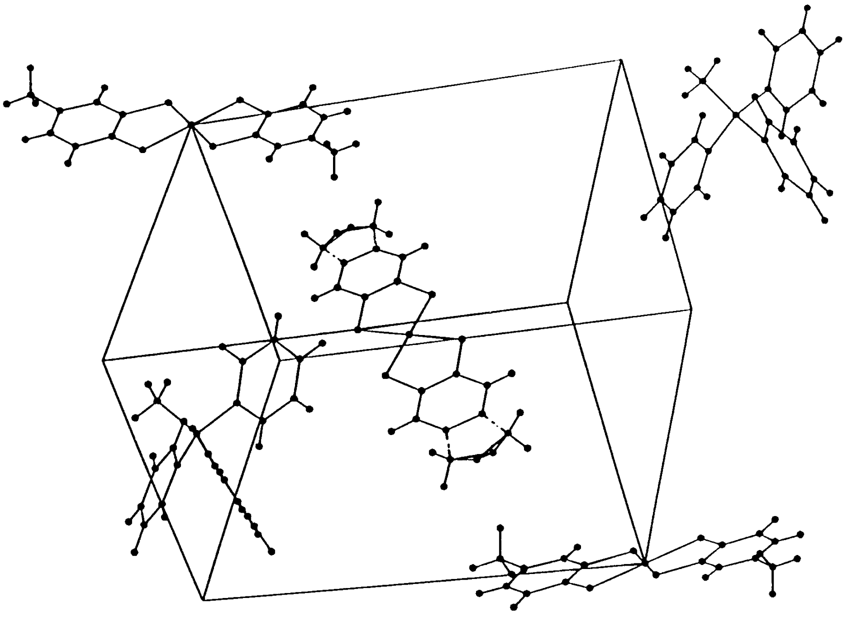

Figure 5. Packing of structure units in the unit cell of (MePh$_3$P)[Ni(tdt)$_2$]·2H$_2$O (**IV**).

Table 3. Crystal data and structure refinement for($(Pr_4N)[Ni(tdt)_2]$ (**III**) and $(MePh_3P)[Ni(tdt)_2]\cdot 2H_2O$ (**IV**).

Compound	**III**	**IV**
Empirical formula	$C_{26}H_{40}NNiS_4$	$C_{33}H_{34}NiO_2PS_4$
Formula weight	553.54	680.52
Temperature	293(2) K	293(2) K
Wavelength	1.54178 Å	0.71073 Å
Crystal system, space group	monoclinic, *Cc*	triclinic, $P\bar{1}$
Unit cell dimensions	a = 24.7240(10) Å b = 7.8100(10) Å c = 17.4570(10) Å α = 90° β = 123.88(1)° γ = 90°	a = 10.029(2) Å b = 10.565(2) Å c = 16.841(3) Å α = 99.21(3)° β = 94.96(3)° γ = 111.72(3)°
Volume	2798.5(4) Å^3	1615.6(5) Å^3
Z; calculated density	4; 1.314 Mg/m^3	2; 1.399 Mg/m^3
Absorption coefficient	3.884 mm^{-1}	0.938 mm^{-1}
F(000)	1180	710
Crystal size (mm)	0.3 × 0.2 × 0.1	0.3 × 0.25 × 0.2
Theta range for data collection	4.31 to 59.95°	1.24 to 22.08°
Index ranges	$0 \leq h \leq 27$ $-8 \leq k \leq 8$ $-19 \leq l \leq 16$	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-17 \leq l \leq 0$
Reflections collected/unique	4000/2125 [R(int) = 0.064]	3998/3857 R(int) = 0.0484]
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2125/2/304	3857/0/382
Goodness-of-fit on F^2	1.035	1.069
Final R indices [$I > 2\text{sigma}(I)$]	$R1$ = 0.0620 $wR2$ = 0.1484	$R1$ = 0.0561 $wR2$ = 0.1471
R indices (all data)	$R1$ = 0.0749 $wR2$ = 0.1613	$R1$ = 0.1052 $wR2$ = 0.1706
Extinction coefficient	0.00027(8)	–
Largest diff. peak and hole	1.089; –0.391 e.Å^{-3}	0.648; –0.654 e.Å^{-3}

Table 4. Selected bond lengths [Å] and angles [°] for $(Pr_4N)[Ni(tdt)_2]$ (**III**) and $(MePh_3P)[Ni(tdt)_2]\cdot 2H_2O$ (**IV**).

III		**IV**	
Ni(1)–S(1)	2.161(3)	Ni(1)–S(1)	2.150(2)
Ni(1)–S(2)	2.158(5)	Ni(1)–S(2)#1	2.150(2)
Ni(1)–S(3)	2.130(4)	Ni(2)–S(3)	2.148(2)
Ni(1)–S(4)	2.151(5)	Ni(2)–S(4)#2	2.136(2)
S(2)–Ni(1)–S(1)	90.3(2)	S(2)–Ni(1)–S(1)	92.01(8)
S(3)–Ni(1)–S(4)	93.2(2)	S(2)#1–Ni(1)–S(1)	87.99(8)
S(4)–Ni(1)–S(1)	88.5(2)	S(4)–Ni(2)–S(3)	91.6(1)
S(3)–Ni(1)–S(2)	80.0(2)	S(4)–Ni(2)–S(3)#2	88.5(1)

Table 5. Possible hydrogen bonding in the $(MePh_3P)[Ni(tdt)_2]\cdot 2H_2O$ (**IV**).

Donor–H [Å]	Donor...Acceptor [Å]	H...Acceptor [Å]	Donor–H...Acceptor [°]
O(2)–H(2B)	O(2)...O(1)	H(2B)...O(1)	O(2)–H(2B)...O(1)
1.1(2)	2.25(3)	1.4(1)	132(2)

The nickel atoms in both structures are almost square planar coordinated (the deviations from NiS_4 least-squares plane are less then 0.01 Å). The NiS_4 least-squares plane is virtually coplanar with the planes of phenyl rings. Almost equal Ni–S bond lengths (range 2.13–2.16 Å) are significantly shorter than the common values for dithiocarbamate complexes (range 2.17–2.18 Å). Since similar results were published [36], we suggest the formal oxidation state III for nickel.

The central atom valence of NiS_4 chromophore calculated using equations (1) and (3) and the constants from Table 1 for the complex **III** is 3.006(1). The calculated valences of Ni(1) and Ni(2) atoms of complex **IV** are equal to 3.009(1) and 3.001(1). Valences of the same atoms calculated with the equation (1) and the formula (2) using program VALMAP [37] are equal to 2.97(3), 2.97(1) and 3.03(1). Both calculations of atomic valences prove the formal oxidation state III of central atoms. We conclude that the arrangement of the nickel inner coordination sphere and the nickel oxidation state in the complexes studied is independent of the nature of the cation. The cations are not bonded to the central atom.

Supplementary data. Crystallographic data for the structures **III**, **IV** reported in this paper are deposited with the Cambridge Crystallographic Data Center (Registry No. CCDC 145944 and 145943).

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REFERENCES

1. Cassoux P., Valade L., Kobayashi H., Kobayashi R., Clark A.R.A. and Underhill A.E., *Coord. Chem. Rev.,* **110**, 115 (1991).
2. Ouahab L., *Coord. Chem. Rev.,* **178-180**, 1501 (1998).
3. Winter C.S., Oliver S.N., Rush J.D., Hill C.A-S. and Underhill A.E., *J. Mater. Chem.,* **2**, 433 (1992).
4. Williams R., Billig E., Waters J.H. and Gray H.B., *J. Am. Chem. Soc.,* **88**, 43 (1966).
5. Walla J., Smékal Z., and Kameníček J., *Acta Univ. Palacki. Olomuc.,* **37**, 61 (1998).
6. Zuo J.L., Xiong R.G., You X.Z. and Huang X.Y., *Acta Cryst.*, **C 52**, 46 (1996).
7. Donnay G. and Allmann R., *Am. Mineral.,* **55**, 1003 (1970).
8. Donnay G. and Donnay J.D.H., *Acta Cryst.*, **B 29**, 1417 (1973).
9. Brown I.D. and Shannon I.D., *Acta Cryst.,* **A 29**, 266 (1973).
10. Brown I.D., *Chem. Soc. Rev.,* **7**, 359 (1978).
11. Brown I.D., The Bond-Valence Method, an Empirical Approach to Chemical Structure and Bonding. In: *Structure and Bonding in Crystals,* Vol. 2 (Eds. M. O'Keefe and A. Navrotsky), Academic Press, N.Y., 1981, p. 1–30 (1981).

12. O'Keefe M., *Struct. Bonding* (Berlin), **71**, 161 (1989).
13. Brown I.D., *Acta Cryst.,* **B 48**, 553 (1992).
14. Brese N.E. and O'Keefe M., *Acta Cryst.,* **B 47**, 192 (1991).
15. Pauling L., *J. Am. Chem. Soc.,* **51**, 1010 (1929).
16. Pauling L., *J. Am. Chem. Soc.*, **69**, 542 (1947).
17. Alternatt D. and Brown I.D., *Acta Cryst.*, **B 41**, 240 (1985).
18. Brown I.D. and Alternatt D., *Acta Cryst.,* **B 41**, 244 (1985).
19. O'Keefe M. and Breese N.F., *J. Am. Chem. Soc.,* **113**, 3226 (1991).
20. Urusov U.S., *Acta Cryst.,* **B 51**, 641 (1995).
21. Thorp H.H., *Inorg. Chem.*, **31**, 1585 (1992).
22. Pidcock E., Collison D. and Garner C.D., *J. Inorg. Biochem.* **51**, 173 (1993).
23. Scarrow R.C., Trimitsis M.G., Buck C.P., Grove G.N., Cowling R.A. and Nelson M.J., *Biochem.,* **33**, 15023 (1994).
24. Scarrow R.C., Brennan B.A., Cummings J.G., Jin H.Y., Duong D.H.J., Kindt J.T. and Nelson M.J., *Biochem.*, **35**, 10078 (1996).
25. Hati S. and Datta D., *J. Chem. Soc. Dalton Trans.,* 1177 (1995).
26. Naskar J.P., Hati S. and Datta D., *Acta Cryst.*, **B 53**, 885 (1997).
27. Valach F., *Polyhedron*, **18**, 699 (1999).
28. Boudreaux E.A. and Mulay L.N., *Theory and Applications of Molecular Paramagnetism*, Wiley, N.Y., p. 491, 1976.
29. Sheldrick G.M., SHELXS-97, enhanced version of SHELX-S, *Acta Cryst.,* **A 46**, 467 (1990).
30. Sheldrick G.M., SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
31. Walker N.P.C. and Stuart D., *Acta Cryst.,* **A 39**, 158 (1983).
32. Nardelli M., PARST-95, *J. Appl. Cryst.,* **28**, 659 (1995).
33. Cambridge Crystallographic Data Centre, Cambridge, UK, 1999.
34. Gmelin Institut für Anorganische Chemie und Fachinformationszentrum FIZ Karlsruhe, Karlsruhe, Germany, 1997.
35. Geary W.J., *Coord. Chem. Rev.,* **7**, 81 (1971).
36. Sellmann D., Binder H., Häussinger D., Heinemann F.W. and Sutter J., *Inorg. Chim. Acta,* **300-302**, 829 (2000).
37. Gonzalez-Platas J. and Gonzalez-Silgo C., Valmap 2.1, Departamento de Fisica Fundamental II, Universitad de La Laguna, Tenerife, Spain, 1999.