Inorganica Chimica Acta, *85* (1984) 83–87

Structure of Tetrakis(2,6-xylyl isocyanide)rhodium(I) 7,7,8,8-Tetracyano-p-quinodimethane, $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]^+(TCNQ^{\cdot-})$*

YASUHIRO YAMAMOTO and HIROSHI YAMAZAKI

Riken (The Institute of Physical and Chemical Research), Wako-Shi, Saitama, 351, Japan

Received July 21, 1983

The title compound, $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]^+(TCNQ^{\cdot-})$, was obtained by the reaction of $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]Cl$ with $Li^+(TCNQ^{\cdot-})$ in acetonitrile. The complex, M. wt. = 831.8, $d_c = 1.31$ g cm^{-3}, crystallizes in the monoclinic space group $P2_1/n$ with a = 15.211(4) Å, b = 19.942(7) Å, c = 14.072(7) Å, β = 98.35(4)°, V = 4223(3) $Å^3$ and Z = 4. The structure consists of mixed stacks of alternating two $Rh(2,6\text{-}Me_2C_6H_3NC)_4$ and two TCNQ molecules. Final refinement yielded R = 0.048 and Rw = 0.055 for 1299 reflections.

Introduction

One-dimensional complexes were found to exhibit anisotropic electronic and magnetic properties [1]. The representative organic systems have been based on the anion of 7,7,8,8-tetracyano-p-quinodimethane [2]. The rhodium isocyanide complexes, $[Rh(RNC)_4]^+$, were found to have the structure which features face to face contact of $[Rh(RNC)_4]^+$ units containing a metal–metal interaction [3]. Recently Iinuma and Tanaka have reported preparations and spectroscopic properties of tetrakis(isocyanide)rhodium(I) cation–TCNQ radical anion salts [4]. They showed on the basis of the spectroscopic studies that the TCNQ molecules were coupled with each other in a columnar structure of $[Rh(RNC)_4]^+(TCNQ^{\cdot-})$. We were interested in the confirmation of the structure and the molecular stacking mode. We report here the structural characterization of $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]^+(TNNQ^{\cdot-})$.

Experimental

Preparation of $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]^+(TCNQ^{\cdot-})$

An acetonitrile solution of $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]Cl$ [5] (0.13 g, 0.20 mmol) was added to a hot acetonitrile solution containing $Li^+(TCNQ^{\cdot-})$ [6] (0.05 g, 0.23 mmol). Dark blue crystals (0.098 g, 60%) precipitated and were filtered. *Anal.* Calcd for $C_{48}H_{40}N_8Rh$: C, 69.31; H, 4.85; N, 13.47. Found: C, 68.78; H, 4.81; N, 13.47. NMR ($CDCl_3$): δ = 2.48(s,Me) and 6.8–7.7 (aromatic protons) ppm. UV (CH_2Cl_2): 849(36150), 830sh, 765(16640), 435sh, 419(24950), 409(25260), 409(25260), 334(41590), and 249(47490)nm.

X-Ray Investigations

An approximate dimension 0.05 × 0.05 × 0.04 mm^3 was used for X-ray data collection on the Rigaku four circle Diffractometer. Intensity data were collected using graphite monochromatized Mo-Kα radiation (λ = 0.7107 Å) and 2θ–ω scan mode at a scan rate of 1° min^{-1}. The intensity decreased rapidly with increasing angles in addition to weak reflections. The intensity data were only of moderate quality, but no decomposition of the sample was observed during data collection. The estimated standard deviations were moderate. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Of 1377 independent reflections in the range $2\theta < 40°$, 1229 reflections with $|F_o| > 3\sigma(F)$ were used in the subsequent calculation. The structure was solved in the space group $P2_1/n$ by the heavy atom method. The Rh atom was located from a Patterson map and other non-hydrogen atoms were located from subsequent Fourier syntheses.

The structure was refined by block-diagonal least squares with anisotropic thermal factors for the non-hydrogen atoms. The final residual factors were R = 0.048 and Rw = 0.055 (w = 1). In the final difference map there were no peaks greater than 0.3 eA^{-3}. Anomalous dispersion effects for Rh were included in the calculation of Fc by using Δf′ and Δf″ [7]. The final atomic coordinates and thermal parameters are listed in Table I. All calculations were made using the UNICS III program [8].

---

*Studies on interactions of isocyanide with transition metal complexes. 25. For the preceding paper, see Y. Yamamoto, Y. Wakatsuki and H. Yamazaki, *Organometallics, 2,* 1604 (1983).

0020-1693/84/$3.00

TABLE I. Final Atomic Coordinates ($\times 10^4$) and Anisotropic Temperature Factor ($\times 10^3$)[a] for $[Rh(2,6\text{-}Me_2C_6H_3NC)_4](TCNQ^{\cdot-})$ with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	377(1)	953(1)	1626(2)	38(1)	47(1)	71(1)	−5(2)	2(1)	1(2)
C10	−27(13)	1900(11)	1643(15)	47(14)	56(17)	51(17)	−10(12)	−11(14)	−1(14)
N10	−231(10)	2452(9)	1635(13)	43(12)	63(14)	68(15)	−4(11)	11(10)	3(12)
C11	−304(14)	3158(11)	1567(16)	56(16)	38(16)	78(20)	19(13)	5(14)	14(15)
C12	483(18)	3499(12)	1449(19)	110(22)	78(19)	65(21)	−25(20)	−38(17)	−5(18)
C13	405(19)	4210(12)	1441(20)	115(20)	63(21)	106(24)	−32(20)	16(18)	−1(20)
C14	−360(20)	4544(15)	1532(20)	161(28)	90(24)	75(23)	−4(21)	10(21)	−13(20)
C15	−1133(17)	4181(13)	1677(18)	127(22)	68(22)	69(20)	5(19)	19(16)	−14(18)
C16	−1113(15)	3446(12)	1656(16)	75(18)	73(19)	33(16)	26(15)	−12(14)	−11(15)
C17	1329(15)	3145(13)	1308(19)	51(17)	96(22)	107(23)	6(16)	13(16)	10(19)
C18	−1934(14)	3017(12)	1809(19)	47(16)	77(20)	132(25)	−13(15)	41(16)	0(19)
C20	1593(14)	1255(12)	1988(18)	51(17)	65(19)	91(21)	−9(13)	13(15)	−4(16)
N20	2338(12)	1357(9)	2252(13)	84(16)	53(14)	68(17)	−3(12)	10(13)	−8(13)
C21	3269(13)	1421(10)	2637(16)	48(16)	24(14)	92(21)	−13(12)	10(14)	−10(14)
C22	3792(15)	1790(12)	2110(18)	71(19)	69(19)	101(23)	−25(16)	39(17)	−26(18)
C23	4709(15)	1816(12)	2559(18)	54(17)	63(19)	116(24)	−5(15)	24(16)	−44(18)
C24	4978(14)	1509(11)	3418(17)	67(18)	38(17)	83(19)	21(13)	2(16)	−8(15)
C25	4390(14)	1160(10)	3959(18)	55(16)	35(18)	98(21)	−1(12)	2(14)	−9(14)
C26	3515(13)	1111(11)	3546(16)	49(14)	70(21)	64(18)	8(14)	8(13)	−2(15)
C27	3418(16)	2120(13)	1160(18)	90(20)	89(21)	76(21)	8(17)	20(17)	39(18)
C28	2845(15)	737(12)	4090(17)	92(19)	89(24)	55(18)	−12(16)	27(15)	1(16)
C30	864(14)	53(12)	1419(16)	54(15)	63(17)	65(18)	−20(14)	7(14)	13(15)
N30	1235(11)	−429(9)	1282(13)	66(13)	74(14)	49(14)	−8(12)	6(11)	12(12)
C31	1779(13)	−992(12)	1138(14)	85(16)	43(15)	46(16)	−10(18)	17(13)	−2(17)
C32	2691(13)	−872(14)	1214(15)	59(15)	95(21)	51(17)	25(18)	11(13)	14(19)
C33	3199(17)	−1491(12)	1049(16)	105(21)	82(21)	40(19)	−4(18)	27(16)	13(16)
C34	2752(16)	−2110(13)	873(18)	87(19)	75(20)	78(21)	2(17)	16(16)	7(18)
C35	1832(17)	−2196(12)	823(18)	110(22)	64(20)	87(22)	23(17)	28(18)	13(18)
C36	1332(18)	−1593(12)	969(17)	141(25)	45(17)	53(20)	10(17)	30(18)	16(16)
C37	3106(16)	−195(13)	1430(17)	87(19)	86(22)	64(20)	3(17)	7(16)	−23(17)
C38	276(16)	−1644(11)	938(18)	70(18)	56(18)	100(22)	−4(15)	21(17)	6(17)
C40	−868(14)	619(11)	1405(15)	62(16)	59(16)	38(16)	−7(13)	5(13)	15(13)
N40	−1587(11)	437(9)	1314(13)	47(12)	63(14)	67(15)	−14(11)	6(11)	8(12)
C41	−2443(13)	172(12)	1215(15)	45(15)	88(21)	34(17)	−17(14)	−1(12)	−11(15)
C42	−3113(15)	650(13)	1325(18)	50(17)	103(23)	86(22)	8(15)	4(15)	28(17)
C43	−4021(14)	361(12)	1168(17)	54(17)	93(21)	62(19)	−1(16)	5(15)	8(17)
C44	−4099(17)	−327(13)	969(19)	85(20)	102(23)	86(23)	−16(18)	−3(18)	15(20)
C45	−3424(15)	−775(13)	945(17)	70(17)	115(27)	66(20)	−21(18)	−5(14)	5(19)
C46	−2570(15)	−520(12)	1065(17)	74(18)	58(18)	68(20)	−9(14)	25(15)	1(16)
C47	−2972(17)	1400(13)	1496(19)	114(23)	55(18)	98(24)	−1(17)	26(19)	−4(18)
C48	−1766(15)	−979(14)	1017(17)	78(17)	60(17)	102(22)	2(20)	8(15)	−2(21)
C51	−193(13)	−129(10)	3842(14)	57(16)	37(15)	46(17)	13(13)	3(14)	2(13)
C52	368(14)	444(10)	3859(15)	67(16)	35(15)	45(16)	1(13)	17(13)	3(13)
C53	30(13)	1072(11)	3947(14)	59(14)	54(18)	33(14)	1(14)	21(11)	−1(14)
C54	−888(14)	1188(10)	3975(17)	58(15)	43(18)	70(19)	9(12)	23(14)	8(14)
C55	−1446(13)	607(10)	3968(15)	50(15)	46(15)	43(16)	−1(12)	15(13)	11(13)
C56	−1134(13)	−42(11)	3884(16)	45(15)	47(15)	73(19)	7(13)	−1(14)	5(15)
C57	−1202(14)	1831(11)	4044(16)	54(16)	50(17)	76(20)	−9(13)	30(15)	0(15)
C58	−649(14)	2404(10)	4028(17)	56(15)	41(15)	79(19)	19(13)	2(14)	−1(15)
C59	−2104(14)	1977(11)	4075(16)	67(17)	51(17)	58(18)	7(14)	21(14)	13(15)
C60	171(13)	−784(10)	3765(15)	51(14)	40(18)	51(17)	−8(12)	5(12)	−4(13)
C61	−361(15)	−1344(12)	3711(17)	59(16)	62(16)	94(25)	15(15)	7(17)	−4(16)
C62	1052(15)	−893(14)	3658(17)	77(17)	87(20)	87(21)	16(19)	24(15)	38(21)
N50	−178(13)	2880(10)	4084(16)	79(15)	87(17)	117(19)	5(14)	19(14)	12(16)
N51	−2878(12)	2074(10)	4068(15)	59(13)	64(15)	123(19)	9(12)	23(13)	−4(15)
N52	−809(14)	−1836(10)	3702(17)	86(16)	70(16)	152(23)	16(14)	−1(16)	3(16)
N53	1788(12)	−916(12)	3565(14)	81(14)	88(16)	93(17)	22(16)	25(12)	9(17)

[a] The form of the anisotropic thermal ellipsoid is $\exp[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*b^* + 2U_{23}klb^*c^*)]$.

Results and Discussion

Structure Description

The molecular structure is a 1:1 salt of [Rh(2,6-$Me_2C_6H_3NC)_4$] cation and TCNQ radical anion, as shown in Fig. 1. The packing mode in the unit cell consists of alterating two [Rh(2,6-$Me_2C_6H_3NC)_4]^+$ and two TCNQ units (Figs. 2 and 3).

Rh(2,6-$Me_2C_6H_3NC)_4$ molecule

The RhC_4 coordination geometry deviates from the best least-squares plane: the dihedral angle between the RhC(10)C(20) and RhC(30)C(40) planes is 10.6(9)°. In contrast, the corresponding coordination geometry of the RhC_4 moiety in [Rh-(2,6-$Me_2C_6H_3NC)_4$](AzaTCNQ) (AzaTCNQ = 4-dicyanomethylene pyridinium dicyanomethylide anion) is reported to be planar [9]. The average Rh–C bond length is 1.96(2) Å, and the N≡C triple bond lengths average 1.14(3) Å, similar to those found in isocyanide complexes. Bond angles at carbon and nitrogen atoms in the RhCNC units deviate slightly from a linear bond angle. A conspicuous feature is that the phenyl ring-20 is considerably tilted by an angle of 63.9(8)° with the RhC(10)C(20) plane and by an angle of 71.7(9)° with the RhC(30)C(40) plane.

The dihedral angles between the other phenyl rings and the RhC(10)C(20) or RhC(30)C(4) plane are smaller (2°–22°) than those between planes containing the Rh atom and phenyl ring-20. The complex forms a stacking structure by avoiding the largely tilted phenyl ring-20 (Tables I–IV).

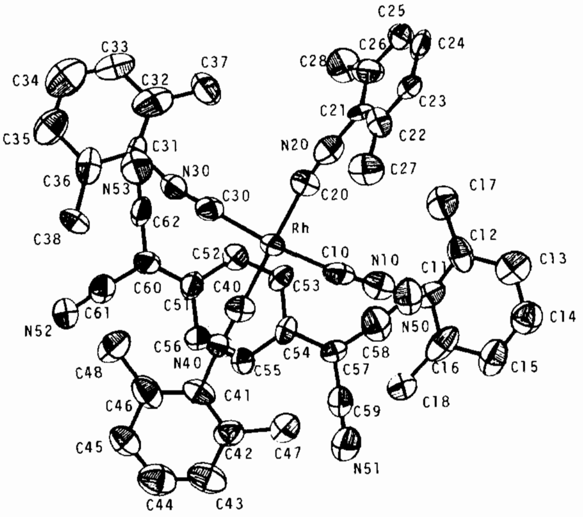

Fig. 1. Molecular structure of [Rh(2,6-$Me_2C_6H_3NC)_4$]-(TCNQ).

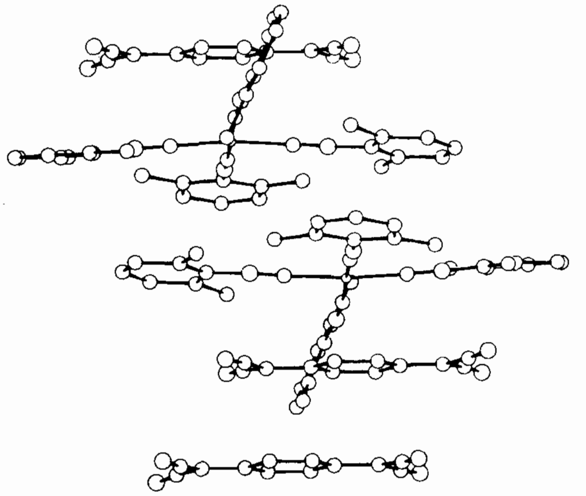

Fig. 2. The stacking arrangement of [Rh(2,6-$Me_2C_6H_3$-$NC)_4]^+(TCNQ^{\cdot-})$.

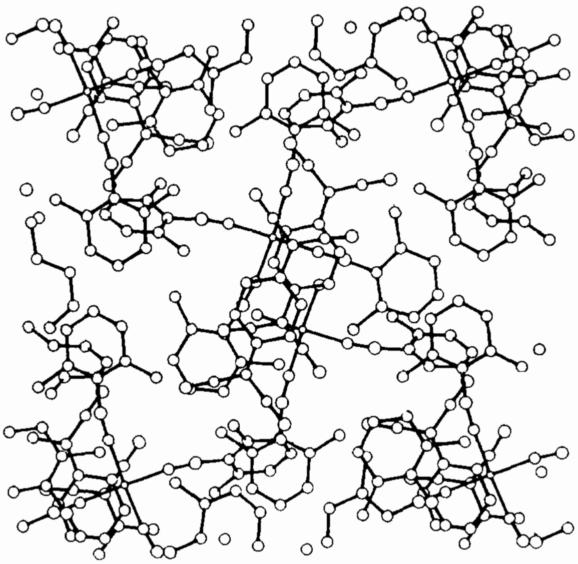

Fig. 3. The stacking arrangement in the crystals of [Rh(2,6-$Me_2C_6H_3NC)_4]^+(TCNQ^{\cdot-})$ as viewed normal to the *ab* plane.

The TCNQ molecule

The quinoid ring of the TCNQ molecule is nearly planar. The distances are not significantly different from those in other TCNQ radical anions [10].

The molecular stacking

The dihedral angles RhC(10)C(20) or RhC(30)-C(40) plane and the quinoid ring are 16.4(9)° or

TABLE II. Crystal Data of [Rh(2,6-$Me_2C_6H_3NC)_4$](TCNQ).

a, Å	15.211(4)
b, Å	19.942(7)
c, Å	14.072(7)
β, deg	98.35(4)
V, $Å^3$	4223.3(29)
Z	4
Space group	$P2_1/n$

TABLE III. Selected Bond Distances (Å) and Angles (°).

(a) Bond distances			
[Rh(2,6-Me$_2$C$_6$H$_3$NC)$_4$]			
Rh–C10	1.99(2)	C30–N30	1.15(3)
Rh–C20	1.94(2)	C40–N40	1.14(3)
Rh–C30	1.98(2)	N10–C11	1.42(3)
Rh–C40	1.99(2)	N20–C21	1.45(3)
C10–N10	1.14(3)	N30–C31	1.43(3)
C20–N20	1.16(3)	N40–C41	1.39(3)
TCNQ			
C51–C52	1.42(3)	C57–C58	1.42(3)
C51–C56	1.45(3)	C57–C59	1.41(3)
C52–C53	1.37(3)	C60–C61	1.37(3)
C53–C54	1.42(3)	C60–C62	1.39(3)
C54–C55	1.44(3)	C58–N50	1.19(3)
C55–C56	1.39(3)	C59–N51	1.19(3)
C51–C60	1.43(3)	C61–N52	1.19(3)
C54–C57	1.38(3)	C62–N53	1.15(3)
Inter- and intra-molecules			
Rh–C52	3.30(2)	C40–C51	3.74(3)
Rh–C53	3.39(2)	C40–C52	3.70(3)
C31–N53	3.42(3)	C40–C53	3.75(3)
C11–N50	3.56(3)	C40–C54	3.79(3)
N40–C55	3.72(3)	C40–C55	3.83(3)
N40–C56	3.71(3)	C40–C56	3.81(3)
C17–C27	3.81(4)	C18–C47	3.59(3)
C21–C37	3.64(3)	C28–C52	3.78(3)
C38–C48	3.59(3)		
(b) Bond angles			
[Rh(2,6-Me$_2$C$_6$H$_3$NC)$_4$]			
C10–Rh–C20	89.2(9)	Rh–C30–N30	172(2)
C20–Rh–C30	87.5(9)	Rh–C40–N40	177(2)
C30–Rh–C40	92.4(9)	C10–N10–C41	168(2)
C40–Rh–C10	91.8(9)	C20–N20–C21	174(2)
Rh–C10–N10	177(2)	C30–N30–C31	174(2)
Rh–C20–N20	172(2)	C40–N40–C41	176(2)
TCNQ			
C58–C57–C59	115(2)	C61–C60–C62	116(2)
C57–C58–N50	175(2)	C60–C61–N52	177(2)
C57–C59–N51	177(2)	C60–C62–N53	173(3)

10.9(8)° respectively. Intermolecular distances between the RhC(30)C(40) plane and the TCNQ molecule fall in the range from 2.71(6) Å (from N(50)) to 4.12(7) Å (from N(52)). The closest bond length of two molecules is 3.30(2) Å of Rh–C(52) bond. The C(40) atom is located at nearly the same distances (3.70–3.83 Å) from six carbon atoms (C(51)–C(56) of the quinoid ring and these atoms form a pseudo-hexagonal pyramid.

The distance of two adjacent rhodium cationic species is *ca.* 3.7 Å. The nearest Rh–Rh bond length is 5.933(3) Å (−x, −y, −z). This is compatible with the fact that the electronic spectrum of this complex does not show any absorption bands at *ca.* 530 nm which present a metal–metal interaction.

The distance between the adjacent TCNQ planes is *ca.* 3.1 Å. This interplanar spacing is in the category of high-conductivity compounds in the simple TCNQ salts [11]. However the electronic conductivity is low (10^{-5} Ω^{-1} cm^{-1}).

This probably arises from the following facts: (1) there is no significant interaction between the π orbitals of TCNQ and the d_{z^2} orbital of the Rh atom since the region of donor–TCNQ overlap does not include the Rh atom, and (2), the Rh(RNC)$_4$–Rh(RNC)$_4$ distance is too large to permit a significant interaction between the d_{z^2} orbitals of the adjacent Rh atoms.

Observed and calculated structure factors as well as a Table (of least-squares planes and dihedral angles) are available from the Editor.

References

1 J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, *20*, 1 (1976).

2 A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, *7*, 232 (1974).

3 (a) K. R. Mann, J. G. Gordon and H. B. Gray, *J. Am. Chem. Soc.*, *97*, 3553 (1975). (b) N. S. Lewis, K. R. Mann, J. G. Gordon and H. B. Gray, *J. Am. Chem. Soc.*,

TABLE IV. Intermolecular Disantaces (Å).

(a) Between TCNQ molecules (<3.4 Å)					
	Symmetry^a			Symmetry^a	
C51–C51	1	3.27(3)	C51–C52	1	3.34(3)
C52–C56	2	3.32(3)	C53–C60	2	3.33(3)
C53–C61	2	3.31(3)	C54–C60	1	3.31(3)
C55–C62	1	3.36(3)	N50–C33	3	3.29(3)
(b) Between Rh(2,6-Me$_2$C$_6$H$_3$NC)$_4$ molecules (<3.6 Å)					
C15–C44	4	3.42(4)	C15–C45	4	3.51(3)
C21–C35	4	3.52(3)	C26–C35	4	3.55(3)
C31–C40	5	3.60(3)	C33–C47	5	3.55(3)

[a] 1: 1 − x, 1 − y, 1 − z; 2: −x, −y, 1 − z; 3: 3/2 − x, 1/2 + y, 1/2 − z; 4: 1/2 − x, 1/2 + y, 1/2 − z; 5: −x, 1 − y, −z.

98, 7461 (1976). (c) V. M. Miskowski, G. L. Nobinger, D. S. Kliger, G. S. Hammond, N. S. Lewis, K. R. Mann and H. B. Gray, *J. Am. Chem. Soc.*, *100*, 485 (1978). (d) K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray and J. G. Gordon, *Inorg. Chem.*, *17*, 828 (1978). (e) H. Endres, N. Gottstein, H. J. Keller, R. Martin, W. Rodemer and W. Steiger, *Z. Naturforsch.*, *34b*, 828 (1979). (f) K. R. Mann, J. A. Thich, R. A. Bell, C. L. Coyle and H. B. Gray, *Inorg. Chem.*, *18*, 2462 (1980). (g) K. Kawakami, M. Okajima and T. Tanaka, *Bull. Chem. Soc. Jpn.*, *51*, 2324 (1978). (h) S. Miya, Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, *21*, 1486 (1982).

4 T. Iinuma and T. Tanaka, *Inorg. Chim. Acta*, *49*, 79 (1981).

5 Y. Yamamoto, K. Aoki and H. Yamazaki, *Inorg. Chem.*, *18*, 1681 (1979).

6 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, *84*, 3374 (1962).

7 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, *53*, 189 (1971).

8 T. Sakurai and K. Kobayashi, UNICS III System (1978).

9 G. Matsubayashi, H. Tanaka, T. Tanaka and K. Nakatsu, *Inorg. Chim. Acta*, *63*, 217 (1982).

10 S. Z. Goldberg, R. Eisenberg, J. S. Miller and A. Epstein, *J. Am. Chem. Soc.*, *98*, 5173 (1976) and therein.

11 Y. Iida, *Bull. Chem. Soc. Jpn.*, *42*, 71 (1969); *ibid.*, *42*, 637 (1969).