Synthesis and X-Ray Structure of Triethylenetetraminepalladium(II) Complex

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(Received July 12, 1976)

The triethylenetetraminepalladium(II) perchlorate and the potassium triethylenetetraminepalladium(II)tris(hexafluorophosphate) were prepared; the X-ray structure analysis has been carried out for the latter compound. The crystal of $[Pd(trien)](PF_6)_2\cdot KPF_6$ is orthorhombic, with space group Pbca: $a=21.645$ (5), $b=20.873$ (5), $c=9.541$ (2) Å, and $Z=8$. The structure has been determined from X-ray diffractometer data and refined to $R=0.091$ (1166 reflections). The Pd atom has a planar coordination of 4N atoms disposed in a somewhat trapezoidal form. The complex cation has a pseudo symmetry plane which is perpendicular to the 4 N plane and bisects the H_2N–Pd–NH_2 angle. In the quadridentate triethylenetetramine ligand, each of the terminal H_2N–CH_2–CH_2–NH– fragments forms a 5-membered chelate ring with the asymmetric envelope conformation, whereas the chelate ring formed by the middle –NH–CH_2–CH_2–NH– fragment has the symmetric envelope conformation. The electronic spectrum of $[Pd(trien)]^{2+}$ is presented.

A number of metal chelates, in particular Co(III) chelates, of the triethylenetetramine (trien) have been prepared and characterized as regards various properties. In 1949 Jonassen *et al.* synthesized the Magnus-type $[Pd(trien)][PdCl_4]$, which was the first isolated salt of the $[Pd(trien)]^{2+}$ ion.[1] However, no detailed studies have yet been made of the complex cation. We report here the synthesis, electronic spectrum, and X-ray structure of the Pd(II) chelate of the trien.

Experimental

Preparation of the Compounds. *$[Pd(trien)](PF_6)_2\cdot KPF_6$*: Triethylenetetramine (58 mg) was added with stirring to a solution of K_2PdCl_4 (107 mg) in 10 ml of water. An orange precipitate was formed but it dissolved immediately. The yellow solution was warmed at 50 °C for 1 h, then $AgPF_6$ (345 mg) dissolved in 5 ml of water was added to the solution. The mixture was stirred for another 0.5 h in the dark and then filtered to remove AgCl. The filtrate was evaporated to dryness under reduced pressure and the residue was dissolved in 10 ml of ethanol. After filtering off the precipitated KPF_6, the filtrate was concentrated to 2 ml, to which 5 ml of water was added. The resulting solution was allowed to stand for 5 days at room temperature. It turned pasty, and yellow needle-like crystals separated out. These crystals were washed with small amounts of cold ethanol and water. Recrystallization was made from ethanol–water solution. Yield, 33%.

Found: C, 9.84; H, 2.40; N, 7.48%. Calcd for $C_6H_{18}N_4PdKP_3F_{18}$: C, 9.92; H, 2.50; N, 7.71%.

$[Pd(trien)](ClO_4)_2$: Triethylenetetramine (202 mg) was added to a solution of $[Pd(NH_3)_4](ClO_4)_2$ (515 mg) in 10 ml of water. The solution was stirred at 50 °C for 2 h and then filtered. The filtrate was evaporated to 5 ml under reduced pressure and the concentrated solution was allowed to stand for 5 days at room temperature. Yellow needle-like crystals were obtained and these were recrystallized from water. Yield, 55%.

Found: C, 15.57; H, 4.12; N, 12.18%. Calcd for $C_6H_{18}N_4PdO_8Cl_2$: C, 15.96; H, 4.03; N, 12.41%.

X-Ray Data Measurement. *Crystal Data*: $C_6H_{18}N_4PdKP_3F_{18}$, F.W.=726.7, Orthorhombic, $a=21.645$ (5), $b=20.873$ (5), $c=9.541$ (2) Å, $U=4311$ (3) Å^3, $D_m=2.18$, $Z=8$, $D_c=2.23$ g cm^{-3}. $\mu(MoK\alpha)=15.0$ cm^{-1}, Mo*Kα* radiation ($\lambda=0.71069$ Å), Space group Pbca. The space group and the approximate cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu*Kα* radiation. The cell dimensions were refined by the least-spuares analysis of 38 θ values accurately measured on a Philips PW 1100 four circle diffractometer with Mo*Kα* radiation.

Data Collection: Intensity data for one octant of the reciprocal space were collected by the ω-2θ scan technique with graphite-monochromated Mo*Kα* radiation; the dimensions of the specimen used were $0.13\times0.10\times0.11$ mm. A scan speed of $0.017°\ s^{-1}$ in ω, a scan width $(0.8+0.2\tan\theta)°$, and stationary background measurements of 20 s were chosen. A total of 1166 reflections having intensity $I_t-2\sqrt{I_t}>I_b$ was collected in the range of $6°\leq2\theta\leq50°$ (I_t: intensity (counts/s) measured at the peak of reflection during the scan; I_b: mean background intensity (counts/s) obtained from preliminary background measurements of 5 s at each side of the scan). The number of the reflections collected is no more than *ca.* 27% of that of the reciprocal lattice points investigated in the data collection. Three standard reflections (10 0 0, 0 8 0, 0 0 2), monitored every 4 h throughout the data collection, showed no significant variation in intensity. Intensity data were processed by the use of the computer program of Hornstra and Stubbe.[2] No absorption correction was applied.

Structure Determination and Refinement. The crystal structure was solved by the heavy atom technique. The positional and thermal parameters were refined by the block-diagonal least-squares method, with anisotropic temperature factors used for Pd, K, and P atoms. The minimized function was $\sum w(F_o-|F_c|)^2$. A weighting scheme of the type suggested by Hughes[3] was applied using $w=0.70$ for $F_o<F_{min}$, $w=1$ for $F_{min}\leq F_o\leq F_{max}$, and $w=(F_{max}/F_o)^2$ for $F_o>F_{max}$; $F_{min}=11.0$ and $F_{max}=31.2$ were found to be optimum. The final R was 0.091 ($R'=[\sum w(F_o-|F_c|)^2/\sum wF_o^2]^{1/2}=0.117$). The temperature factors for lighter atoms, especially those for F atoms, are rather high. This is indicative of the disorder in the arrangment of those atoms. In the final cycle of the refinement all parameter shifts were $<(1/5)\sigma$. The atomic coordinates and the temperature factors are listed in Table 1, along with their estimated standard deviations. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7702).

Atomic scattering factors of neutral Pd, P, F, N, and C, and K^+ were taken from Ref. 4. The real part of the anomalous dispersion correction was applied for the Pd atom. Computer programs used in the calculations were as follows: RSSFR-4 (Fourier synthesis), HBLS-4 (least-squares calculation), and DAPH (interatomic distances and angles, least-squares

TABLE 1. THE ATOMIC COORDINATES AND TEMPERATURE FACTORS

	x	y	z	B/Å^2
Pd	0.1521(1)	0.1000(1)	0.1658(3)	a)
N(1)	0.222(1)	0.122(1)	0.026(3)	5.0(5)
N(2)	0.139(1)	0.022(1)	0.048(3)	5.3(6)
N(3)	0.088(1)	0.065(1)	0.286(3)	5.7(6)
N(4)	0.156(1)	0.173(1)	0.315(3)	5.5(5)
C(1)	0.226(1)	0.063(2)	−0.077(3)	6.0(8)
C(2)	0.197(1)	0.006(2)	−0.012(4)	6.1(8)
C(3)	0.103(2)	−0.025(2)	0.124(4)	7.1(9)
C(4)	0.072(2)	0.001(2)	0.245(4)	8.0(1.0)
C(5)	0.098(2)	0.087(2)	0.428(4)	8.2(1.0)
C(6)	0.110(1)	0.157(2)	0.430(4)	6.0(8)
K	0.4121(3)	0.2526(4)	0.3696(7)	a)
P(1)	0.0313(3)	0.1700(3)	−0.1442(9)	a)
P(2)	0.2781(4)	0.3037(4)	0.1424(9)	a)
P(3)	0.4008(5)	0.0898(5)	0.1602(11)	a)
F(1)	−0.009(1)	0.223(1)	−0.085(3)	13.4(9)
F(2)	−0.022(1)	0.146(1)	−0.240(3)	10.0(6)
F(3)	0.019(1)	0.117(1)	−0.039(3)	13.3(9)
F(4)	0.088(1)	0.191(1)	−0.053(3)	10.3(6)
F(5)	0.048(1)	0.219(1)	−0.263(3)	10.1(6)
F(6)	0.073(2)	0.120(2)	−0.210(4)	16.5(1.1)
F(7)	0.240(1)	0.263(1)	0.033(2)	8.6(5)
F(8)	0.258(1)	0.367(1)	0.076(3)	11.7(7)
F(9)	0.338(1)	0.294(1)	0.064(3)	12.0(7)
F(10)	0.295(1)	0.237(1)	0.221(3)	12.0(7)
F(11)	0.217(1)	0.307(1)	0.240(3)	9.7(6)
F(12)	0.315(1)	0.338(1)	0.253(3)	11.2(7)
F(13)	0.451(1)	0.058(1)	0.071(2)	9.3(6)
F(14)	0.424(1)	0.047(1)	0.290(3)	12.0(8)
F(15)	0.351(1)	0.119(1)	0.256(3)	13.8(8)
F(16)	0.374(1)	0.131(2)	0.038(3)	14.2(9)
F(17)	0.447(1)	0.143(1)	0.200(3)	14.7(9)
F(18)	0.353(1)	0.036(1)	0.128(3)	13.0(8)

a) Anisotropic temperature factors (× 10^4) in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$, with parameters:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	27.5(5)	21.5(4)	139(3)	−13(1)	29(3)	−14(3)
K	27(2)	35(2)	117(10)	−7(4)	15(7)	34(9)
P(1)	22(2)	17(2)	122(11)	4(3)	7(9)	17(8)
P(2)	21(2)	31(2)	115(11)	8(4)	1(9)	−34(9)
P(3)	43(2)	37(3)	158(13)	20(5)	26(13)	−14(13)

planes, and coordinates of H atoms), all of which were adapted to the FACOM 270—30 computer at Osaka City University.

In order to confirm the structure, further least-squares calculations were carried out by the use of the anisotropic temperature factors for all atoms, here the weighting scheme $w=(7.6+F_o+0.013F_o^2)^{-1}$ was employed. The R and R' reached 0.054 and 0.072, respectively. The difference Fourier map calculated at this point showed no peaks$>$0.55 e Å^{-3}. Of the residual peaks, nine could be identified as H atoms.

Electronic Spectra and Electric Conductivity. The absorption spectra were recorded at room temperature using a Hitachi EPS-3T Recording Spectrophotometer. The electric conductivity was measured in water by means of an MY-8 apparatus of the Yanagimoto Seisakusho, Ltd.

Results and Discussion

The projection and elevations of the complex cation are shown in Figs. 1 and 2, respectively. The Pd atom is surrounded by 4 N atoms disposed in trapezoidal form. The complex has a pseudo mirror plane which is perpendicular to the plane defined by the 4 N atoms and bisects the N(1)–Pd–N(4) angle. The 5-membered chelate rings A and C assume the asymmetric envelope conformation, whereas the middle ring B has the symmetric one: the –NH–CH$_2$–CH$_2$–NH– fragment in B has an almost eclipsed conformation, with the torsional angle of 9°. This conformation of the trien ligand is essentially identical with that found in [Cu(SCN)-(trien)](NCS),[5] though the corresponding torsional angle in the Cu complex (49°) is rather large as compared with that of the Pd complex. In the present [Pd-(trien)]$^{2+}$ all C atoms lie on the upper side of the 4 N plane, while the Pd atom deviates slightly downward from the plane, by 0.06 Å. The F(4) atom is in close contact with the Pd atom, at a distance of 3.15 Å. The equations of some least-squares planes are given in Table 2.

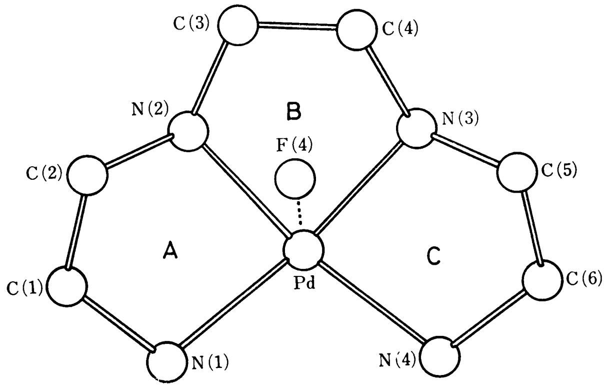

Fig. 1. Projection of the [Pd(trien)]$^{2+}$.

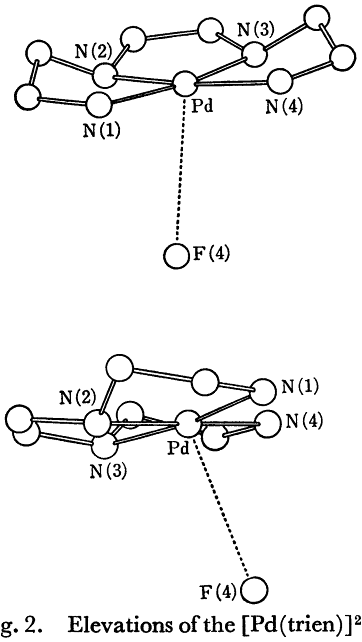

Fig. 2. Elevations of the [Pd(trien)]$^{2+}$.

Table 2.

1) Equations of planes in the form $AX+BY+CZ=D$[a)]

	A	B	C	D
Plane (1)				
N(1), N(2), N(3), N(4)	−0.668	0.514	−0.538	−2.03
Plane (2)				
N(1), C(1), C(2)	−0.884	0.260	−0.389	−3.68
Plane (3)				
N(2), C(2), C(1)	−0.452	−0.209	−0.867	−1.85
Plane (4)				
N(2), C(3), C(4)	−0.800	0.211	−0.563	−2.56
Plane (5)				
N(3), C(4), C(3)	−0.727	0.355	−0.588	−2.56
Plane (6)				
N(3), C(5), C(6)	−0.980	0.163	0.112	−1.33
Plane (7)				
N(4), C(6), C(5)	−0.751	0.135	−0.646	−3.99

2) Deviations (l) of atoms from the plane (1)

	l/Å		l/Å
N(1)	−0.01	C(1)	−0.16
N(2)	0.01	C(2)	−0.69
N(3)	−0.01	C(3)	−0.37
N(4)	0.01	C(4)	−0.26
Pd	0.05	C(5)	−0.66
		C(6)	−0.08

3) Torsional angles (ϕ) in N-C-C-N fragments

	ϕ/°
N(1)-C(1)-C(2)-N(2)	47
N(2)-C(3)-C(4)-N(3)	9
N(3)-C(5)-C(6)-N(4)	47

a) The X, Y, and Z coordinates in Å are referred to the crystallographic axes.

Table 3. Bond lengths (l) and angles (ϕ)

	l/Å		ϕ/°
Pd-N(1)	2.07(2)	N(1)-Pd-N(2)	86(1)
Pd-N(2)	2.00(3)	N(2)-Pd-N(3)	85(1)
Pd-N(3)	1.95(3)	N(3)-Pd-N(4)	85(1)
Pd-N(4)	2.08(2)	N(4)-Pd-N(1)	104(1)
N(1)-C(1)	1.57(4)	Pd-N(1)-C(1)	105(2)
N(2)-C(2)	1.42(4)	Pd-N(2)-C(2)	107(2)
N(2)-C(3)	1.44(4)	Pd-N(2)-C(3)	110(2)
N(3)-C(4)	1.43(5)	Pd-N(3)-C(4)	111(2)
N(3)-C(5)	1.45(5)	Pd-N(3)-C(5)	108(2)
N(4)-C(6)	1.53(4)	Pd-N(4)-C(6)	108(2)
C(1)-C(2)	1.49(5)	N(1)-C(1)-C(2)	111(3)
C(3)-C(4)	1.44(6)	N(2)-C(2)-C(1)	110(3)
C(5)-C(6)	1.48(5)	N(2)-C(3)-C(4)	113(3)
		N(3)-C(4)-C(3)	117(3)
Pd···F(4)	3.15(3)	N(3)-C(5)-C(6)	111(3)
		N(4)-C(6)-C(5)	108(3)
P-F	1.51—1.62(4)		

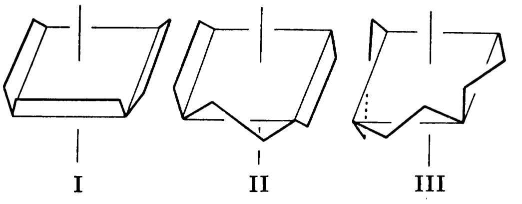

Fig. 3. Possible conformers for a planar disposition of the trien ligand.

Bosnich *et al.* studied the strain energy in the metal chelates of the trien which has a planar disposition. They suggested that the most stable conformations of the ligand are those shown in Figs. 3 I and II.[6)] The conformer I has C_s symmetry, while the symmetries of the conformers II and III are C_2. The conformations of trien in the Pd and Cu complexes can be classified as I. The conformation II has not yet been found in the crystal structures of the trien complexes. Although the conformer III was predicted to be less stable than I and II, it is believed that in (+)$_D$-*trans*-[CoCl$_2$(trien)]$^+$ the chelating ligand assumes the conformation III.[7)]

The bond lengths and angles are given in Table 3. The N(1)-Pd-N(4) bond angle is somewhat larger than 90°, showing considerable strain in the complex. However, it is comparable to those in the [Cu(SCN)(trien)](NCS) (98.9°)[5)] and (−)$_D$-*trans*-[Co(NO$_2$)$_2$(L-3,8-dimetrien)](ClO$_4$) (101.6°).[8)] The bond length of Pd-N (primary amino group) seems to be somewhat longer than that of the Pd-N (secondary): the mean value of the former is 2.08 Å, whereas that of the latter is 1.98 Å. However, such a difference in metal-nitrogen bonds is less pronounced in the Co complex,[8)] and is not found in the Cu one.[5)]

The crystal structure viewed down the c axis is shown in Fig. 4. A K$^+$ ion is surrounded octahedrally by 6 PF$_6^-$ ions, 10F atoms of which are in contact with the K$^+$ ion at distances varying from 2.64 to 3.27 Å. There are some weak N-H···F hydrogen bonds in the crystal. The N···F distances are listed in Table 4, along with some important interatomic distances. Both of the NH$_2$

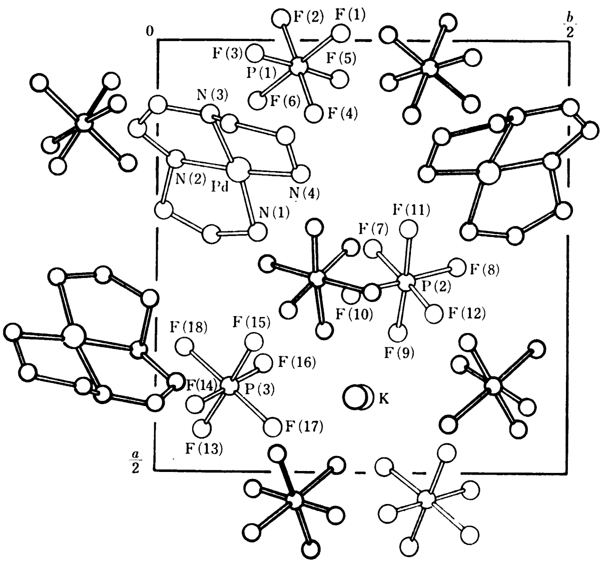

Fig. 4. Crystal structure of the [Pd(trien)](PF$_6$)$_2$·KPF$_6$ viewed down the c axis. Atoms drawn by thin lines are those of the equivalent position (x,y,z), while those shown by the thick lines belong to (x, 1/2−y, 1/2+z).

Table 4. Selected interatomic distances (l)

Atom A	Atom B	l/Å of A B	l/Å of H···B	Positions[a] of A	Positions[a] of B
N(1)-H[b]	F(7)	2.97(3)	2.24	1	1
N(1)-H	F(11)	3.12(3)	2.30	1	4
N(4)-H	F(7)	3.07(3)	2.29	1	4
K	F(1)	3.24(3)		1	2
K	F(1)	2.74(3)		1	3
K	F(2)	2.84(3)		1	2
K	F(5)	3.16(3)		1	2
K	F(9)	2.64(3)		1	4
K	F(10)	2.93(3)		1	1
K	F(12)	2.98(3)		1	1
K	F(15)	3.27(3)		1	1
K	F(16)	3.02(3)		1	4
K	F(17)	2.90(3)		1	1

a) Numerals refer to the following equivalent positions: 1: (x, y, z); 2: ($1/2+x, 1/2-y, -z$); 3: ($1/2+x, y, 1/2-z$); 4: ($x, 1/2-y, 1/2+z$). b) The coordinates of the H atoms were calculated on the assumption that the N–H bond length is 1.03 Å.

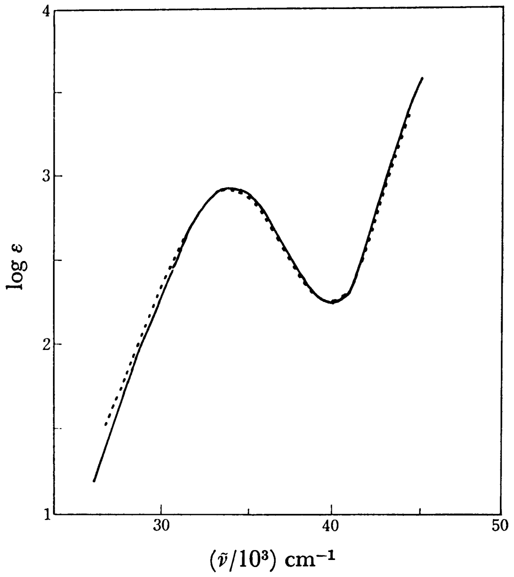

Fig. 5. Absorption spectra of the Pd(II) complexes of trien in aqueous solutions. [Pd(trien)](PF$_6$)$_2$·KPF$_6$: ——; [Pd(trien)](ClO$_4$)$_2$: ------.

groups participate in the hydrogen bonding, while none of the –NH– groups do.

Figure 5 shows the electronic spectra of the triethylenetetraminepalladium(II) perchlorate and the potassium triethylenetetraminepalladium(II) tris(hexafluorophosphate) in an aqueous solution. These spectra agree with each other and indicate that the species in the solution are identical. The spectra of these compounds resemble those of [Pd(NH$_3$)$_4$](ClO$_4$)$_2$[9] and [Pd(R-pn)$_2$]Cl$_2$.[10] Accordingly, on the basis of D$_{4h}$ symmetry the absorption band at 33.7×10^3 cm^{-1} may be assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g, and $^1B_{1g}$.[9] The peak position of the trien complex is almost equal to that of the ammine complex, but is displaced to a slightly lower energy relative to the band maximum of the R-pn complex. However, the absorption in the present complexes is about three times as intense as those in the complexes cited for comparison. The ion pairing which gives a 5-coordinate complex sometimes results in an enhancement of the absorption intensity.[11] The molar conductance of the perchlorate is 250 ohm^{-1} cm^2 mol^{-1} at 25 °C in 5.90×10^{-4} M aqueous solution. The concentration of this solution is almost equal to those of the solutions used for the measurements of the spectra. The value of conductance is typical for a 1 : 2 electrolyte: there seems to be no appreciable interaction between the cation and the anion in 10^{-3}—10^{-4} M solution.

The PdN$_4$ chromophore in the [Pd(NH$_3$)$_4$]$^{2+}$ and [Pd(R-pn)$_2$]$^{2+}$ have an effective symmetry of D$_{4h}$, and therefore the d→d transition is Laporte-forbidden. On the other hand, the configuration of 4 N atoms in the [Pd(trien)]$^{2+}$ is trapezoidal and the symmetry of the chromophore can be regarded as C$_{2v}$. Since this group contains no inversion center, Laporte's rule is relaxed. Furthermore, symmetry considerations imply that the C$_{2v}$ symmetry is favorable to the mixing of d→d transitions with some allowed transitions through configuration interaction, as compared with the case of D$_{4h}$ symmetry. Some of these might be responsible for the enhancement of the intensities in the ligand fields bands. The orbitals in the plane of the ligator atoms are most sensitive to the change of the disposition of these atoms. Consequently, the intensity of the $a_1(d_{xy}) \rightarrow b_1(d_{x^2-y^2})$ transition may be the most enhanced of the d→d transitions.

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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