Inorganica Chimica Acta, 22 (1977) 209–213
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis of Mixed Complexes of Ruthenium(II) with 2,2'-Dipyridyl

R. A. KRAUSE

Department of Chemistry, University of Connecticut, Storrs, Ct. 06268, U.S.A.

Received August 31, 1976

A simple, reliable method has been developed for producing solutions of $[Ru(dipy)(py)_4]^{2+}$ *(dipy = 2,2'-dipyridyl; py = pyridine). This reagent has been employed to prepare mixed ligand complexes with o-phenanthroline (phen), ethylenediamine (en), 2-aminomethylpyridine (PMA), and 2-aminoethylpyridine (PEA). Complexes which have been isolated are* cis- *and* trans-$[Ru(dipy)_2py_2](ClO_4)_2$, cis- *and* trans-$[Ru(dipy)(py)_2(phen)](ClO_4)_2$, $[Ru(dipy)(phen)_2](ClO_4)_2$, $[Ru(dipy)(py)_2en](ClO_4)_2$, $[Ru(dipy)(py)_2(PMA)](ClO_4)_2$, $[Ru(dipy)(PMA)_2](ClO_4)_2$, *and* $[Ru(dipy)(py)_2(PEA)](ClO_4)_2$. *The infrared spectra of these complexes have been found to be quite useful in identifying and characterizing them; their electronic spectra are reported.*

Introduction

In recent years there have been an increasing number of reports on the chemistry of ruthenium. This is certainly due to a number of factors, of which the observed catalytic activity of some of these compounds, the study of emission spectra of ruthenium complexes, and the observation of rather interesting chemistry in many instances are important. Our interest in these last two areas caused us to prepare a number of complexes derived from one parent substance, $[Ru\,dipy\,(py)_4]^{2+}$.

This complex was first reported by Dwyer, Goodwin and Gyarfas [1]; we have prepared several new complexes by replacement of two or more coordinated pyridines with dipyridyl (*cis-* and *trans-*isomers), *o*-phenanthroline (*cis-* and *trans*-isomers), ethylenediamine, 2-aminomethylpyridine and 2-aminoethylpyridine. These complexes are described below.

Experimental

Measurements

Ultraviolet–visible spectra were obtained on a Cary 14 spectrophotometer using acetonitrile (Aldrich 99%) solutions. Infared spectra were obtained on mineral oil mulls between NaCl plates using a Perkin Elmer Infracord spectrophotometer (correcting with polystyrene standardization). Molar conductances of acetonitrile solutions ($10^{-3}M$) were obtained at 25.0 °C using an Industrial Instruments, Inc. conductivity bridge, Model RC 16 B2.

Materials

All chemicals were reagent grade except as noted. $RuCl_3 \cdot 3H_2O$ (39.00% Ru) was obtained from J. Bishop & Co., Malvern, Pa. 2,2'-Dipyridyl (dipy), 1,10-phenanthroline (phen), 2-aminomethylpyridine (PMA), 2-aminoethylpyridine (PEA), and ethylenediamine (en) were obtained from Aldrich Chemical Co., Milwaukee, Wisc. 53233.

Preparation of Compounds

All analyses were performed by Baron Consulting, P.O. Box 663, Orange, Ct. 06477.

$[Ru(dipy)Cl_4]$.

Our procedure is an improvement over that originally reported by Dwyer *et al.* [1] in that ours is a one step procedure, readily scaled up. To 50.0 ml of 1.00 N HCl is added 10.30 g $RuCl_3 \cdot 3H_2O$ and 7.55 g dipy (20% excess over one equivalent). After stirring to dissolve the solids the container is stoppered, allowed to stand for several days, and the product isolated by filtration, washing with water. It is dried *in vacuo* over P_4O_{10}. Yields increase with time; isolation after seven days gives 70%, while after 24 days 91% is obtained. Longer times are not advantageous, the yield only increasing to 93% at 2½ months.

$[Ru(dipy)(py)_4]^{2+}$ *stock solution*

Ten grams of $[Ru(dipy)Cl_4]$ is mixed with 600 ml water, 180 ml ethanol and 20 ml pyridine and refluxed for 24 hours. At this time the solution is orange–brown. After filtration to remove boiling chips the solution is diluted to one liter; aliquots are evaporated to dryness (steam bath or rotary evaporator), rinsed with ether to remove excess pyridine, and this residue utilized as starting material in the succeeding preparations.

$[Ru(dipy)(py)_4](ClO_4)_2$ could be isolated from this solution by evaporating 200 ml of stock to low volume, dilute to 100 ml with water, bring to boiling and add 10 ml pyridine. Then to the boiling solution is added 10 ml of 10% aqueous $NaClO_4$; precipitation starts at once. After cooling the orange solid is isolated by filtration, washed with water and dried *in vacuo* over P_4O_{10}, yielding 2.63 g (68%). *Anal.* Calcd for $[Ru(dipy)(py)_4](ClO_4)_2$: C, 46.63; H, 3.65; N, 10.88. Found: C, 46.27; H, 3.77; N, 10.90%. $\Lambda_M = 347\ \Omega^{-1}\ cm^{-1}$.

Recrystallization from 10% aqueous ethanol generally resulted in a compound displaying a poorer analysis; the unrecrystallized samples appear to be quite clean.

$[Ru(dipy)(py)_2(en)](ClO_4)_2$

The residue from 200 ml of stock solution is mixed with 100 ml water and 4 ml ethylenediamine and placed on the steam bath. After two hours the hot solution is filtered to remove a trace of $[Ru(py)_4Cl_2]$, reheated and 30 ml of 10% aqueous $NaClO_4$ added to precipitate the complex. Filtration after 24 hours followed by washing (water) and drying *in vacuo* over P_4O_{10} yields 2.25 g (67%) of crude sample. Recrystallization from 80 ml of 10% ethanol (under Ar) yields 1.45 g red–brown needles. *Anal.* Calcd for $[Ru(dipy)(py)_2en](ClO_4)_2$: C, 39.17; H, 3.89; N, 12.46; Cl, 10.51. Found: C, 39.19; H, 3.98; N, 12.38; Cl, 10.31%. $\Lambda_M = 335\ \Omega^{-1}\ cm^{-1}$.

$[Ru(dipy)(py)_2(PMA)](ClO_4)_2$.

The residue from 50 ml of stock solution was mixed with 25 ml water, 5 ml ethanol and 0.14 g PMA. After 3 hours on the steam bath the solution was filtered, 10 ml 10% $NaClO_4$ added to the hot solution and the product isolated as above the following day in 84% yield (0.76 g). Recrystallization from 10% ethanol (40 ml per gram) under Ar gave dark purple crystals (67% yield). *Anal.* Calcd for $[Ru(dipy)(py)_2(PMA)](ClO_4)_2$: C, 43.22; H, 3.63; N, 11.69. Found: C, 43.30; H, 3.61; N, 11.89%. $\Lambda_M = 332\ \Omega^{-1}\ cm^{-1}$.

$[Ru(dipy)(PMA)_2](ClO_4)_2$

The residue from 50 ml of stock solution is mixed with 30 ml water, 3 ml ethanol, and 1 ml PMA and refluxed 5 days. After filtration 10 ml of 10% $NaClO_4$ solution is added to the hot solution and the complex is isolated the following day as above in 82% yield (1.82 g). This material gives an acceptable analysis; it may be recrystallized from 10% ethanol (25 ml per gram) in 64% recovery. *Anal.* Calcd for $[Ru(dipy)(PMA)_2](ClO_4)_2$: C, 39.29; H, 3.60; N, 12.50; Cl, 10.55. Found: C, 39.04; H, 3.54; N, 12.53; Cl, 10.65%. $\Lambda_M = 337\ \Omega^{-1}\ cm^{-1}$.

$[Ru(dipy)(py)_2(PEA)](ClO_4)_2$.

The residue from 200 ml of stock solution is mixed with 100 ml water, 10 ml ethanol, and 0.56 g PEA and placed on the steam bath for four hours. After filtration 30 ml of 10% $NaClO_4$ is added to the hot solution and the product isolated as above the following day in 83% yield (3.07 g). Recrystallization from 10% ethanol (under Ar) (about 40 ml per gram) gives 50% recovery. *Anal.* Calcd for $[Ru(dipy)(py)_2(PEA)](ClO_4)_2$: C, 44.02; H, 3.83; N, 11.41. Found: C, 44.55; H, 3.71, N, 11.09%. $\Lambda_M = 298\ \Omega^{-1}\ cm^{-1}$.

cis- *and* trans-*$[Ru(dipy)(py)_2(phen)](ClO_4)_2$.*

The residue from 200 ml of stock solution is mixed with 40 ml ethanol, 40 ml water and 1.00 g $phen \cdot H_2O$ (one equivalent). After 24 hours on the steam bath the solution is filtered and 20 ml of 10% $NaClO_4$ added; the product is isolated as above in 95% yield (3.78 g). The mixture of isomers is heated with 200 ml 10% ethanol (under Ar). The residue is pure *trans* isomer. *Anal.* Calcd for $[Ru(dipy)(py)_2(phen)](ClO_4)_2$: C, 48.36; H, 3.30; N, 10.58; Cl, 8.92. Found: C, 48.59; H, 3.30; N, 10.62 Cl. 8.90%. $\Lambda_M = 341\ \Omega^{-1}\ cm^{-1}$. This compound may be recrystallized from 10% ethanol (480 ml per gram) with 40% recovery.

The filtrate from this residue yields 1.68 g (42% of theoretical) of *cis* isomer slightly contaminated with *trans. Anal.* Found: C, 48.48; H, 3.35; N, 10.35%. $\Lambda_M = 343\ \Omega^{-1}\ cm^{-1}$. Because of solubility properties we were unable to completely remove the *trans*-isomer from the *cis.*

$[Ru(dipy)(phen)_2](ClO_4)_2$.

The residue from 100 ml of stock solution is mixed with 80 ml water, 40 ml ethanol and 1.00 g phen H_2O (2 equivalent). After refluxing for seven days the solution is filtered, precipitated with 20 ml 10% $NaClO_4$ and isolated as above yielding 1.94 g (95%). If the solution is only refluxed for two days the product is contaminated with *trans* $[Ru(dipy)(py)_2(phen)](ClO_4)_2$ or occasionally by both *cis* and *trans* isomers. Recrystallization from 10% ethanol (under Ar) (145 ml per gram) yields a 66% recovery of the pure complex. *Anal.* Calcd for $[Ru(dipy)(phen)_2](ClO_4)_2$: C, 50.00; H, 2.96; N, 10.29. Found: C, 50.07, 49.69; H, 3.33, 3.06; N, 10.58, 10.33%. $\Lambda_M = 350\ \Omega^{-1}\ cm^{-1}$. The absorption spectrum of this compound is identical with that of the same complex described by Bosnich [2].

cis- *and* trans-*$[Ru(dipy)_2(py)_2](ClO_4)_2$.*

The residue from 100 ml of stock solution is mixed with 50 ml water, 10 ml ethanol and 0.39 g dipy (one equivalent) and placed on the steam bath. Filtration after 24 hours followed by addition of 10 ml 10% $NaClO_4$ and isolation as above yields 1.70 g

(88%) of the mixture of isomers. This solid is recrystallized from 100 ml of 10% ethanol (under Ar). The residue is extracted with two additional 100 ml portions of this solvent yielding 0.58 g of residue, *trans*-$[Ru(dipy)_2(py)_2](ClO_4)_2$. *Anal.* Calcd for $[Ru(dipy)_2(py)_2](ClO_4)$: C, 46.75; H, 3.40; N, 10.91. Found: C, 47.26; H, 3.61; N, 10.98%. $\Lambda_M = 339$ Ω^{-1} cm^{-1}.

The first extraction (above) on slow cooling yields 0.58 g of the *cis* isomer. Found: C, 46.87; H, 3.65; N. 10.76%. $\Lambda_M = 348$ Ω^{-1} cm^{-1}.

Results and Discussion

Syntheses

Our initial attempts to duplicate Dwyer, Goldwin and Gyarfas' results were not entirely successful. This could very well be due to a difference in purity of the ruthenium starting material. We have now devised a simple procedure, which we feel to be quite reproducible, for the synthesis of a series of ruthenium(II) complexes based on the parent ion $[Ru(dipy)py_4]^{2+}$.

The original work by Dwyer, Goodwin and Gyarfas [1] required several steps to arrive at solutions of this complex. The precursor to the tetrapyridine complex, $[Ru(dipy)Cl_4]$, we prepare directly from $RuCl_3 \cdot 3H_2O$; while Dwyer *et al.* make mention of obtaining a material in this fashion they do not report having utilized it in syntheses. Recently James and McMillan [3] reported the synthesis of $K[Ru(dipy)Cl_4]$ as a potential intermediate but again, they require the prior synthesis of another compound; they do not report on further reactions of this complex.

Dwyer *et al.* showed that $[Ru(dipy)py_4]^{2+}$ could undergo a number of substitutions; we have found this to be quite general, preparing several new complexes reported here, including the separation of two pairs of *cis–trans* isomers. Dwyer's group utilized a pyrolysis procedure to convert $(dipy-H)[Ru(dipy)Cl_4]$ into $[Ru(dipy)_2Cl_2]$ [4]. We have been able to simply add dipy to solutions of $[Ru(dipy)(py)_4]^{2+}$ to obtain $[Ru(dipy)_2(py)_2]^{2+}$ in a much more straightforward fashion; furthermore, our technique yields both *cis*- and *trans*-isomers.

During the conversion of $[Ru(dipy)(py)_4]^{2+}$ to $[Ru(dipy)(phen)_2]^{2+}$ we observed the slow reaction to procede in steps. First, $[Ru(dipy)(py)_2phen]^{2+}$ was formed as a mixture of isomers. Then, one of these isomers converted to $[Ru(dipy)(phen)_2]^{2+}$ yielding a mixture of this complex and $[Ru(dipy)(py)_2phen]^{2+}$ (identified by the infrared spectra of solid products – below). The isomer reacting first was assigned the *cis* configuration. Finally, after several days refluxing, even the remaining *trans* isomer was converted to the tris-chelate. Structures were assigned to *cis*- and *trans*-$[Ru(dipy)_2py_2](ClO_4)_2$ by comparing their infrared spectra with those of the above complexes (next section).

Complete substitution of pyridine could also be accomplished with PMA yielding $[Ru(dipy)(PMA)_2]^{2+}$. PEA may give a complex of this type but we could only isolate oils from this reaction. Extended reaction of the starting material with ethylenediamine yielded clumps of black crystals which analyze for $[Ru(dipy)en_2](ClO_4)_2$. However, further study (chromatography, NMR, and luminescence measurements to be reported later) show this "compound" to be a mixture of at least three components. Complete characterization awaits future work.

All of the compounds reported here gave satisfactory analyses. Molar conductances were in the expected range for the electrolyte type present.

Other than Dwyer, Goodwin and Gyarfas' original paper [1] there have been very few reports of ruthenium complexes containing one dipyridyl and different coligands. Complexes of the type $[Ru(AA)O_\eta]$ (where AA is dipyridyl or *o*-phenanthroline) have been reported by Ishiyama [5–7] and Ishiyama and Koda [8]; similar substances containing hydroquinone and methanol have been reported by Ishiyama [9]. Bosnich has reported the synthesis, resolution and CD spectrum of $[Ru(dipy)(phen)_2](ClO_4)_2^2$ [2]. Complexes of the type currently being reported (*i.e.*, with one dipyridyl and other bidentate amines) do not appear to have been prepared previously.

Infrared Spectra

All of the complexes show the expected peaks for the groups they contain (*e.g.* NH_2, ClO_4^- modes). A few of the bands were found to be very useful for characterization. In addition to the weak, sharp 1600 cm^{-1} dipyridyl peak indicating the presence of this ligand, the ring adjacent hydrogen modes were found to be very useful (see Table I). Bands near 760 and 730 cm^{-1} are characteristic of dipyridyl, while those near 755 and 700 cm^{-1} belong to pyridine.

The strong band at 840 cm^{-1} serves to indicate the presence of *o*-phenanthroline; another phen mode near 718 is less useful since many of the complexes containing none of this ligand show a band here. Our assignments are in agreement with those of Schilt and Taylor [10]. The weak absorptions near 740 and 718 cm^{-1} were not particularly useful for characterization.

It was the 700 cm^{-1} band in these compounds which first indicated the occurrence of isomerism. In Figure 1 are shown spectra (700 region only) of a mixture of the isomers before recrystallization and the separated isomers for a representative example. The spectra themselves are far more informative than any tabulation of data. It should also be noted that

TABLE I. Infrared Bands of Complexes in the 700 cm^{-1} Region.

Band Assignment		dipy	py	dipy	dipy			py
$Rudipy_3Cl_2$		759 s		740 w	725 m			
$Rupy_4Cl_2$			756 s					684 s
$Rudipypy_4(ClO_4)_2$		764 s	757 s	740 w	729 w	718 m	702 m	
$Rudipypy_2en(ClO_4)_2$		764 sh	755 s		730 m		700 m	693 sh
$Rudipyen_2(ClO_4)_2$		761 s		747 w	729 m			
$Rudipypy_2(PEA)(ClO_4)_2$		760 sh	754 s		726 m			695 m,b
$Rudipypy_2(PMA)(ClO_4)_2$		766 sh	755 s		730 m			698 m,b
$Rudipy(PMA)_2(ClO_4)_2$		763 sh	757 s		727 m			
trans-$Rudipy_2py_2(ClO_4)_2$	807 w	767 s	758 s	740 w	729 m	718 w,b		696 m
cis-$Rudipy_2py_2(ClO_4)_2$		762 sh	753 s	740 w	728 m		703 m	
trans-$Rudipypy_2phen(ClO_4)_2$	807 w	768 s	758 m	740 w	732 m	719 m		688 m
cis-$Rudipypy_2phen(ClO_4)_2$		765 sh	757 s		730 m	719 m	703 m	690 sh
$Rudipy(phen)_2(ClO_4)_2$		763 s			728 m	717 s		

TABLE II. UV–Visible Spectra of Ruthenium(II) Complexes in CH_3CN. Peak maxima in kK (molar $\epsilon \times 10^{-3}$).

$[Rudipy(py)_4]^{2+}$	21.9 (5.5)	23.0 sh (4.7)	28.8 (14)	34.5 (32)		41.0 (27)
trans-$[Rudipy(py)_2(phen)]^{2+}$	21.0 (11)	21.1 sh	24.8 (6.2)	35.1 (29)	37.7 (29)	40.7 (31)
cis-$[Rudipy(py)_2(phen)]^{2+}$	22.3 (9.6)	23.4 (9.3)	30.1 (11)	34.7 (37)	37.4 (37)	40.8 (24)
trans-$[Ru(dipy)_2(py)_2]^{2+}$	21.1 (8.6)	22.2 (7.6)	29.8 (12)	34.8 (52)		41.2 (24)
cis-$[Ru(dipy)_2(py)_2]^{2+}$	22.2 (7.9)		29.8 (12)	34.7 (53)		41.2 (24)
$[Rudipy(phen)_2]^{2+}$	22.6 (18)	23.6 (17)	31.9(sh) (7.7)	35.3 (43)	38.0 (91)	
$[Rudipy(py)_2PMA]^{2+}$	21.5 (6.0)		28.8 (14)	34.5 (32)		41.7 (20)
$[Rudipy(PMA)_2]^{2+}$	20.9 (assym.) (6.5)		27.8 (12)	34.1 (35)	34.8 sh	40.6 (20)
$[Rudipy(py)_2PEA]^{2+}$	22.0 (5.5)		29.3 (3.2)	34.6 (34)		41.2 (22)
$[Rudipy(py)_2en]^{2+}$	21.0 (broad) (4.0)		27.2 (13)	34.2 (32)	35.0 sh	41.8 (17)

the *trans* isomers (only) exhibit a weak peak at 807 cm^{-1}; this is most likely an overtone (or combination mode) for the more symmetrical D_{4h} (or "pseudo D_{4h}" *trans*$[Ru(dipy)(py_2)(phen)]^{2+}$) RuN_6 group frequency probably located in the 400 cm^{-1} region.

Splitting in the 700 cm^{-1} region in pyridine complexes was first ascribed by Rao to the occurence of isomerism [11]. However, Gill *et al.* [12] felt this was more likely due to lattice effects. Our separation of two different components each with unsplit bands shows this to be due to isomerism.

It will be noticed from the presence of a weak shoulder at 690 in *cis*-$[Ru(dipy)(py_2)phen]^{2+}$ that a small *trans* impurity remains, even after repeated recrystallizations.

Using Dwyer, Goodwin and Gyarfas' pyrolysis procedure and then preparing $[Ru(dipy_2)(py_2)]$-$(ClO_4)_2$ [4] we have only obtained the *cis* isomer. This may be the reason for these authors not discovering *cis–trans* isomerism in these complexes.

Electronic Spectra

Spectral data for the complexes prepared are listed in Table II; some representative spectra appear in Figure 2. The molar extinction coefficients are all much higher than conventional values for d–d transi-

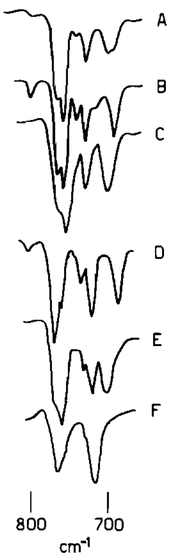

Figure 1. Infrared Spectra in the 700 cm^{-1} region of A) Crude [Ru(dipy)$_2$(py)$_2$](ClO$_4$)$_2$; B) *trans*-[Ru(dipy)$_2$(py)$_2$](ClO$_4$)$_2$; C) *cis*-[Ru(dipy)$_2$(py)$_2$](ClO$_4$)$_2$; D) *trans*-[Ru(dipy)(py)$_2$phen](ClO$_4$)$_2$; E) *cis*-[Ru(dipy)(py)$_2$phen](ClO$_4$)$_2$; F) [Ru(dipy)(phen)$_2$](ClO$_4$)$_2$.

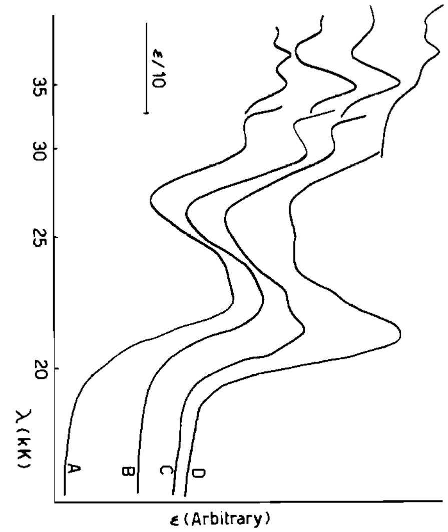

Figure 2. Absorption spectra of complexes in CH$_3$CN. A) *cis*-[Ru(dipy(py)$_2$phen](ClO$_4$)$_2$; B) *cis*-[Ru(dipy)$_2$(py)$_2$](ClO$_4$)$_2$; C) *trans*-[Ru(dipy)$_2$(py)$_2$](ClO$_4$)$_2$; D) *trans*-[Ru(dipy)(py)$_2$phen](ClO$_4$)$_2$.

tions. However, in studying the circular dichroism of [Ru(dipy)(phen)$_2$]$^{2+}$ Bosnich has pointed out that the lower energy band probably contains d–d components as well as metal–ligand charge transfer [2]. Thus, we anticipate some d–d character to be present in the lowest energy band of the complexes under study; both *cis*-[Ru(dipy)$_2$(py)$_2$]$^{2+}$ and *cis*-[Ru(dipy)(py)$_2$phen]$^{2+}$ bear a strong resemblance to each other in this band. Likewise, both *trans*-[Ru(dipy)$_2$(py)$_2$]$^{2+}$ and *trans*-[Ru(dipy)(py)$_2$phen]$^{2+}$ bear a close resemblance in their degree of splitting of this lowest energy band. Since the higher energy bands appear to be ligand $\pi \rightarrow \pi^*$ [2], and presumably are uninfluenced by the complexes' symmetry, these similarities in the lowest bands appear to reflect the molecular geometry and thus most likely are a combination of d–d and charge transfer.

Bosnich has assigned the higher energy bands as ligand $\pi \rightarrow \pi^*$ and obtained good agreement with his model on this basis. The higher extinction coefficients for the shorter wavelength bands in the present complexes is in keeping with their assignment as inter-ligand transitions.

References

1 F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem.*, *16*, 42 (1963).
2 B. Bosnich, *Inorg. Chem.*, *7*, 2379 (1968).
3 B. R. James and R. S. McMillan, *Inorg. Nucl. Chem. Letters*, *11*, 837 (1975).
4 F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem.*, *16*, 544 (1963).
5 T. Ishiyama, *Ann. Rep. Rad. Center Osaka*, *8*, 40 (1967).
6 T. Ishiyama, *Bull. Chem. Soc. Japan*, *42*, 2071 (1969).
7 T. Ishiyama, *Bull. Chem. Soc. Japan*, *44*, 1571 (1971).
8 T. Ishiyama and Y. Koda, *Inorg. Chem.*, *11*, 2837 (1972).
9 T. Ishiyama, *Bull. Chem. Soc. Japan*, *48*, 443 (1975).
10 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, *9*, 211 (1959).
11 G. S. Rao, *Naturwiss.*, *46*, 556 (1959).
12 N. S. Gill, R. H. Nuttall, D. W. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, *18*, 79 (1961).