

THE EFFECT OF PYRIDINE AND ITS DERIVATIVES ON THE ACTIVITY OF COBALT-BROMIDE CATALYSTS*

M. HRONEC and V. VESELÝ

*Department of Chemistry and Technology of Petroleum,
Slovak Institute of Technology, 880 37 Bratislava*

Received July 16th, 1976

Complexes CoBr_2L_2 , where the ligand L is pyridine or some of its derivatives, are distinguished by high catalytic activities in the oxidation of alkylaromates in acetic acid as solvent. The activities decreased in the order pyridine > isoquinoline > quinoline \gg acridine. Methyl groups in the α - and α' -positions influenced the activity, whereas in the γ -position no effect was observed. We have also studied in detail the dependence of catalytic activity on the molar ratio Co : Br : Py in the region 1 : 0-4 : 0-8. The increase in oxidation rate and in yield of trimesic acid due to the presence of pyridine exhibited a maximum. The increase was highest where the ratio Co : Br was the lowest. At ratios Py : Co > 4 the oxidation was retarded and yields of trimesic acid decreased, but no induction period was observed. On the basis of spectra measured in the visible region the formation of various cobalt bromide complexes is discussed.

The preceding papers of this series describe the effects of aliphatic and aromatic amines on the oxidation of mesitylene catalysed by salts of cobalt and bromine in acetic acid as solvent. These effects which were generally activating, proved considerably affected by further substituents in the amine molecules and by their spatial arrangement. Conductance and spectral measurements have shown that a number of amines react, in acetic acid, with cobalt dibromide with the formation of new cobaltous complexes, having one or more ligands of the amine in the coordination shell. Compared to the ordinary cobalt-bromide catalysts, the catalytic activity of these catalysts is many times higher.

The coordination of an amine to the complex also modifies its function in the process of the radical reaction. Thus many aromatic amines incorporated into a cobalt bromide complex lose their original antioxidative effect and moreover activate the catalyst. If coordination of the amine with cobalt bromide is not possible, *e.g.* for steric reasons, the amine exerts its independent influence. Then, if it is an inhibitor of radical reactions, the oxidation of a hydrocarbon is retarded and the induction period increased. Further measurements have shown that ligands activating the cobalt bromide catalysts are even certain heterocyclic compounds. As will be

* Part VII in the series Oxidation of Polyalkylated Aromatic Hydrocarbons; Part VI: This Journal 42, 1851 (1977).

shown in this communication, pyridine and some of its derivatives are particularly efficient in this respect.

EXPERIMENTAL

Reagents. All liquid nitrogen compounds were re-distilled. Acridine and picolinic acid were re-crystallized. Pyridine hydrobromide (PyH.Br) was prepared by treatment of pyridine with an excess of hydrobromic acid. The complexes CoBr_2L_2 , where L denotes a pyridine derivative, were prepared in butanol by mixing cobalt dibromide with an excess (10–20%) of the nitrogen compound¹. The complex $\text{CoBr}_4(\text{PyH})_2$ was prepared by mixing solutions of cobalt dibromide and pyridine hydrobromide in butanol in the stoichiometric ratio². All the complexes synthesized were crystallized from alcohol and tested for purity by elemental analysis. The cobalt-mono-bromide complex designated $\text{Co}(\text{OAc})\text{Br}$ was synthesized from cobaltous acetate and hydrogen bromide in acetic anhydride³. The other chemicals were purified as described in the preceding paper.

Spectral measurements. Electron spectra were recorded with a Specord apparatus (Zeiss, Jena), 0.5 to 5 cm thermostated cells being employed.

Conductance measurements. The change in conductance associated with the interaction of cobalt bromide with a nitrogen compound in acetic acid was followed as described⁴. The oxidation procedure was the same as in the preceding paper.

RESULTS

From the large number of heterocyclic nitrogen compounds we selected the relatively stable ones. Polycyclic compounds, as well as compounds with more than two atoms of nitrogen in a ring, were not sufficiently resistant to oxidation under the given reaction conditions, formed brown deposits, in some cases even inhibited oxidation.

The most active nitrogen compound of all we studied was pyridine. The activity of the cobalt-bromide complex was several times higher than that of the dibromide itself. In consequence of great reaction rates high yields of trimesic acid were obtained in short reaction times. Piperidine, as its hydrogenated derivative, was less efficient (Fig. 1). Nevertheless, the decrease in reaction rate could be compensated for by extending the reaction time; thus an aromatic tricarboxylic acid was obtained in a yield of 81.7 mol% (Table I). Morpholine influenced the reaction rate like piperidine, but owing to inferior selectivity of the reaction the yield of trimesic acid was a mere 70.3 mol%, despite the long reaction time.

As has been mentioned, a considerable increase in activity of cobalt-bromide catalysts can be reached if they are coordinated with ligands containing nitrogen donor atom. In the oxidation of mesitylene catalysed by cobalt-bromide complexes CoBr_2L_2 where L denotes a pyridine derivative, the activity of a complex was controlled by interaction of the central cobalt atom with the nitrogen compound. As can be seen from Fig. 2, the activity was reduced with those pyridine derivatives where steric hindrance interfered. A methyl group at an α -position affected the activity, but

if bound to the γ -position no effect was observed. Thus the effects of α -picoline and 2,4-lutidine were equal, but different from that of 2,6-lutidine. The activity of the complexes decreased markedly in the ligand order pyridine-quinoline-acridine, but there was no difference between pyridine and isoquinoline, or between pyridine and β -picoline. The difference between quinoline and isoquinoline, as well as the differences between the pyridine derivatives, in their effect on catalytic activity of the cobalt-bromide complexes may be due to steric reasons.

The steric effect, as one strongly affecting the catalytic activity, is also well apparent with pyridinecarboxylic acids. A carboxyl group bound to the *ortho* position

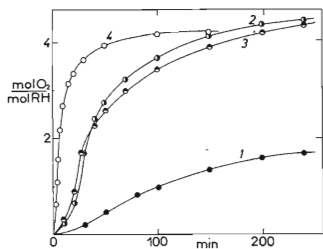


FIG. 1

Effects of Piperidine 2, Morpholine 3 and Pyridine 4 on the Oxidation of 1:23M Mesitylene in Acetic Acid at 140°C and 11 atm Catalysed by $1.82 \cdot 10^{-2}$ M-CoBr₂·6H₂O

The molarity of nitrogen compounds was $3.65 \cdot 10^{-2}$ mol/l; 1 absence of a nitrogen compound.

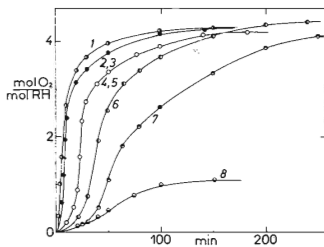


FIG. 2

Oxidation of Mesitylene Catalysed by Complexes CoBr₂L₂ in Acetic Acid

The ligands were: 1 pyridine, 2 β -picoline, 3 isoquinoline, 4 α -picoline, 5 2,4-lutidine, 6 2,6-lutidine, 7 quinoline, 8 acridine. Reaction conditions as in Fig. 1.

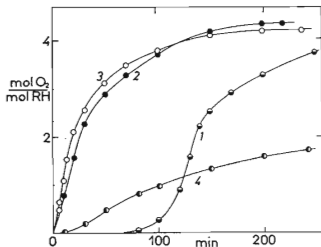


FIG. 3

Effects of Pyridine Derivatives on the Activity of Cobalt Dibromide

Conditions as in Fig. 1. 1 2-Bromopyridine, 2 nicotinic acid, 3 nicotinamide, 4 picolinic acid.

shields the nitrogen atom and allows formation of chelate structures. As can be seen from Fig. 3, as a result of these effects, picoline acid in a molar ratio to cobalt of 2 : 1 had virtually no influence on the oxidation rate of mesitylene in acetic acid at a temperature of 140°C. The course of the reaction and the yield of trimesic acid were practically the same as with cobalt dibromide alone (Fig. 1). Nicotinic acid, by contrast, was a strong activator, but weaker than pyridine or β -picoline. The lower activity of nicotinic acid is probably due to the steric and the electron-accepting effects of the carboxyl group, since the chelate formation is not significant

TABLE I

Effects of Pyridine and its Derivatives on Yield of Trimesic Acid in the Oxidation of Mesitylene in Acetic Acid Catalysed by Cobalt Dibromide or its Complexes CoBr_2L_2

Experimental conditions: 140°C, 11 atm, concentrations in mol/l: mesitylene 1.23, CoBr_2 or CoBr_2L_2 $1.82 \cdot 10^{-2}$, nitrogen compound $3.65 \cdot 10^{-2}$. The complexes CoBr_2L_2 were used in experiments 4, 5, 9, 10 and 11.

Experiment	Nitrogen compound	Reaction time min	Yield of aromatic acid mol %	
			5-methyl- isophthalic	trimesic
1	—	210 ^a	8.4 ^b	1.2
2	morpholine	295	6.1	70.3
3	piperidine	250	5.1	81.7
4	pyridine	145	5.9	83.8
5	α -picoline	180	5.4	79.7
6	β -picoline	140	5.1	79.2
7	2,4-lutidine	185	4.9	79.1
8	2,6-lutidine	270	4.9	79.3
9	quinoline	260 ^a	18.1	53.9
10	isoquinoline	175	3.9	77.1
11	acridine	165 ^c	not analyzed	
12	2-bromopyridine	250	4.5	76.6
13	picolinic acid	265 ^a	10.8 ^d	2.1
14	nicotinic acid	255	4.9	77.1
15	nicotinamide	220	6.6	78.1
16	($\text{CoBr}_2 + \text{HBr}$)	250 ^e	18.6	65.8
17	$\text{Co}(\text{OAc})_2^{\dagger}$ 2-bromopyridine	330 ^f	4.7	80.2

^a The oxidation still continued, ^b yield of 3,5-dimethylbenzoic acid was 53.9 mol%, ^c oxidation ceased after consumption of c. 1 mol of O_2 per mol of mesitylene, ^d yield of 3,5-dimethylbenzoic acid was 50.6 mol%, ^e catalysed by a mixture of CoBr_2 ($1.82 \cdot 10^{-2}\text{M}$) and 37% aqueous HBr ($3.65 \cdot 10^{-2}\text{M}$), ^f catalysed by a mixture of $\text{Co}(\text{OAc})_2$, 4 H_2O ($1.82 \cdot 10^{-2}\text{M}$) and 2-bromopyridine ($3.65 \cdot 10^{-2}\text{M}$).

in this case; this is suggested by the identical oxidation courses in the presence of nicotinic acid and nicotinamide.

A different effect was observed with 2-bromopyridine. Despite the bulkiness of the bromine atom, bound to the *ortho* position, the decrease in activity was not such as with picolinic acid. An explanation of this is the impossibility of formation of chelate structures, which are catalytically inferior. In addition, as has been pointed out in many papers, bromine compounds are efficient activators of cobalt catalysts. This is also demonstrated by the oxidation of alkylaromates in acetic acid catalysed by cobaltous acetate, which was markedly accelerated by the presence of 2-bromopyridine (Table I). A drawback of this bromo derivative is a rather long induction period. Then, however, the oxidation gives high yields of trimesic acid.

We have paid much attention to the activating effect of pyridine in relation to the molar ratio Co : Br : Py. This dependence was studied in a range of 1 : 0–4 : 0–8. If the molar ratio of Co to Br was lower than 1 : 2 under the given reaction conditions and in the absence of pyridine the oxidation rates were low but with increasing concentration of bromine the rate of oxidation rose fast. It was found that in the presence of pyridine the oxidation rates of mesitylene increased at any molar ratio of cobalt to bromine. As can be seen from Fig. 4, the yield of trimesic acid increased too. It should be pointed out, however, that the increase in oxidation rate and in yield of trimesic acid caused by the presence of pyridine passes through a maximum and the increase is highest at the lowest molar ratio of Co to Br. If this ratio was 1 : 0,

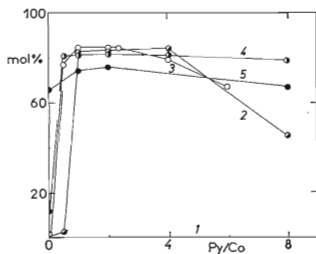


FIG. 4

Yield of Trimesic Acid in Relation to Molar Ratio of Pyridine to Cobalt at the Following Molar Ratios of Co : Br, 1 : 0, 2 : 1 : 0.5, 3 : 1 : 1, 4 : 1 : 2, 5 : 1 : 4

Conditions as in Fig. 1.

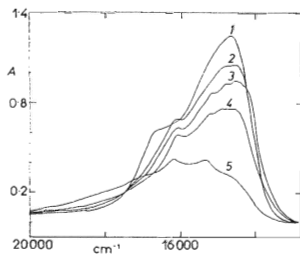


FIG. 5

Effect of Pyridine Concentration on the Electron Spectrum of Cobalt Dibromide in Acetic Acid at 60°C. Cell thickness 1 cm. Concentrations in mol/l : CoBr₂ 4.0 · 10⁻³; Py 1 0; 2 4.0 · 10⁻³; 3 8.0 · 10⁻³; 4 1.2 · 10⁻²; 5 4.0 · 10⁻².

i.e. in the absence of bromides, the effect of pyridine was the same as that of the other nitrogen compounds, *i.e.* negative. Fig. 1 shows that catalysts having a molar ratio $\text{Co} : \text{Br} = 1 : 2$ or lower were little active for the preparation of tricarboxylic acids in the absence of pyridine under the given experimental conditions. This is why their industrial production is conducted at elevated temperatures or higher concentrations of bromine, and in some cases is promoted by the synergic effect of other metals.

As is seen from Fig. 4 and Table I, high yields of trimesic acid can be obtained even in the absence of pyridine if the concentration of bromine is higher. The same catalytic activity, and thus the same yields of aromatic carboxylic acids, can be reached at a considerably lower concentration of bromine if an optimum amount of pyridine is added. Thus catalysts with $\text{Co} : \text{Br}$ ratios $1 : 0.5$ or $1 : 1$, as well as the complex catalyst $\text{Co}(\text{OAc})\text{Br}$, were little active in the absence of pyridine and even after 5 hours' oxidation practically no tricarboxylic acid was formed. By the addition of pyridine to these catalysts to attain a ratio of $\text{Co} : \text{Py} = 1 : 1$ to $1 : 2$ their activities increased several times and trimesic acid was obtained in yields over 80 mol%. At high concentrations of pyridine, the ratio of Py to Co being higher than 4, the oxidation was retarded and yields of trimesic acid decreased. The oxidation rate and yields of the acids were the lower, the lower was the concentration of bromine in the system. In contrast to the use aromatic amines, the induction period was absent even at high concentrations of pyridine. This can be accounted for by the difference in the effect of these compounds on a radical reaction: in the absence of a metallic catalyst aromatic amines are more or less efficient inhibitors, whereas pyridine and some of its derivatives are not.

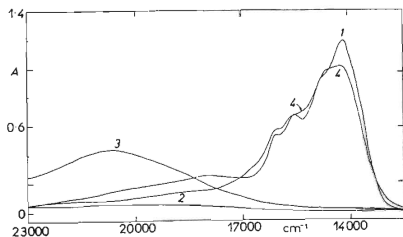


FIG. 6

Electron Spectra of Complexes of Cobalt Dibromide with Picolinic Acid in Acetic Acid

Cell thickness 1 cm. 20°C Concentrations in mol/l: CoBr_2 $1.6 \cdot 10^{-2}$; picolinic acid $1.3 \cdot 10^{-2}$, $2.6 \cdot 10^{-2}$, $3.1 \cdot 10^{-1}$. Curve 4 refers to a solution containing CoBr_2 ($2 \cdot 10^{-3}$ mol/l) and pyridine hydrobromide ($2 \cdot 10^{-3}$ mol/l) at 60°C in a 0.5 cm cell.

The mechanism of action of nitrogen compounds is associated with their effect on the formation of catalytically active complexes. The changes occurring in the reaction of cobalt dibromide with pyridine and its derivatives in acetic acid can easily be followed, *e.g.* by measuring the spectra in the visible region (Figs 5 and 6).

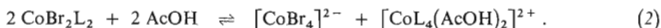
DISCUSSION

The preceding papers of this series have shown that coordination of nitrogen ligands into a complex with cobalt bromide activates the cobalt–bromine linkage, which mediates the electron transfer between an aromatic hydrocarbon and the metal complex. The result is a marked increase in oxidation rate and yield of the aromatic polycarboxylic acid.

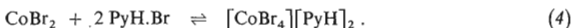
We have now found that the catalytic activities are equal if a complex is used, *e.g.* CoBr_2L_2 , or a mixture of cobalt dibromide and pyridine (or a derivative of the latter) in a suitable ratio. This makes possible a simple and rapid preparation of the catalysts, even such catalysts which are rather labile when in contact with air.

The complexes of metal halides with pyridine and its derivatives have been described in detail^{5–8}. Their stability is given by steric and electronic effects in the complex formation. Substitution in the α -position, especially if combined with one in the α' -position, of pyridine reduces the stability of the complexes^{9–11} and weakens the Co–Br bond in the CoBr_2L_2 complexes¹². In the oxidation of mesitylene substitution in the α -position decreased the oxidation rate.

Reactivity of complexes is strongly influenced by physical, but mainly by chemical properties of the solvent. Their effects can alter their structures or even give rise to new complexes. The complexes CoBr_2L_2 are no exception; on dissolution in acetic acid they undergo the following reactions

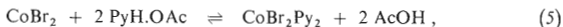


The formation of ionic complexes CoBr_4^{2-} in acetic acid was followed by spectral and conductance measurements⁴. Since at room temperature these complexes are poorly soluble and separate from the solution we studied the reaction of cobalt dibromide with pyridine at a temperature of 60°C, at which no precipitation occurred. As is apparent from Fig. 5, electron spectra suggest formation of the complex CoBr_4^{2-} (ref.⁷). It is formed by the consecutive reactions (3) and (4):



The decrease in absorbance of the band of cobalt dibromide in the region 14000 to 15000 cm^{-1} with increasing concentration of pyridine can be explained on the basis of the following assumptions.

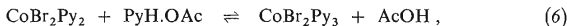
Pyridine in acetic acid is present in the ionic form PyH.OAc , which undergoes reactions (3) and (4), giving rise to the complex $[\text{CoBr}_4][\text{PyH}]_2$. The complex CoBr_2Py_2 may be formed simultaneously by reaction (5),



but undergoes transformation according to reactions (1) and (2). The complexes CoBr_2 , CoBr_2Py_2 and CoBr_4^{2-} have tetrahedral structures and exhibit absorption bands in the region 17000–13500 cm^{-1} . We assume that at 60°C, at which temperature the complex CoBr_4^{2-} does not precipitate from the solution, an equilibrium is established between these, and possibly other cobalt complexes. It remains to determine their proportion at given temperatures and concentrations. At 20°C, as a result of the precipitation, the complex CoBr_4^{2-} prevails, but with increasing temperature may be transformed, e.g. by the reversible reactions (1) and (2).

However, the decrease in absorbance at 14650 cm^{-1} with increasing pyridine concentration testifies to the formation of complexes whose total absorbance is smaller than that of cobalt dibromide. According to our measurements, as well as the reported data^{13,15}, the molar absorptivities ϵ of the complexes CoBr_4^{2-} at 14650 cm^{-1} are approximately $1000\text{M}^{-1}\text{cm}^{-1}$. The molar absorptivity of CoBr_2Py_2 in nitromethane at 15500 cm^{-1} and 25°C was reported¹⁴ as $\epsilon = 525\text{M}^{-1}\text{cm}^{-1}$, and that of cobalt dibromide in acetic acid¹⁵ at 20°C as $310\text{M}^{-1}\text{cm}^{-1}$. The molar absorptivities of complexes CoBr_2Py_3 and CoBr_2Py_4 are much lower⁷. If pyridine and cobalt dibromide in acetic acid formed exclusively the complex $[\text{CoBr}_4][\text{PyH}]_2$ (reactions (3) and (4)), the absorbance at 14650 cm^{-1} would have to increase. It must be borne in mind, however, that reaction (3) also produces cobaltous acetate so that the complex CoBr_4^{2-} can never exceed half the concentration of cobalt dibromide. Despite this fact the absorbance of the band at 14650 cm^{-1} should increase in the presence of pyridine, as a consequence of the great differences in molar absorptivities of these complexes. Spectrum 2 in Fig. 5 and spectrum 4 in Fig. 6 show that despite a two-fold concentration of cobalt dibromide and a two-fold optical path in the cell the absorbance failed to increase, so that the complex CoBr_4^{2-} must have been formed in a far lower concentration. In case only reaction (5) occurred, giving rise to the complex CoBr_2Py_2 , still the absorbance should not take such a steep decrease.

In the presence of a solvent capable of coordination, such as acetic acid, or at higher concentrations of pyridine the tetrahedral complex CoBr_2Py_2 may be transformed by reactions (6) and (7) into a five-coordinate intermediate CoBr_2Py_3 and an octahedral complex CoBr_2Py_4 :



The molar absorptivities of these are considerably lower. Spectrum 5 in Fig. 5 reveals that at higher concentrations of pyridine there appeared low-intensity bands at 19100 cm^{-1} , 18350 cm^{-1} and 17400 cm^{-1} , associated with the octahedral complex⁷ CoBr_2Py_4 .

The results described above illustrate the possible transformations of cobalt complexes in acetic acid by the action of pyridine or its derivatives. Kinetic measurements showed that the maximum catalytic activity and the maximum yields of trimelic acid (Fig. 4) were obtained at molar ratios of $\text{Py} : \text{Co} = 1 : 1$ to $2 : 1$, above the ratio $4 : 1$ the activity decreased. This decrease was probably due to the formation of cobalt complexes with coordination sites occupied by the pyridine ligands, which impeded substitution reactions in the course of oxidation. The mechanism of reaction and the structures of the active complexes will be dealt with in more detail in our subsequent papers.

Pyridinecarboxylic acids, as ligands with two different donor atoms, reacted with cobalt dibromide in a more complex way. In the addition of picolinic acid to a solution of cobalt dibromide up to a ratio of 2 mol per gramatom of cobalt a light blue precipitate separated at 20°C . This, unlike the stable pyridine complex $[\text{CoBr}_4][\text{PyH}]_2$, is labile in contact with air, but as be seen from spectrum 1 in Fig. 6 the electron spectrum of a saturated solution can be ascribed to the complex¹³ CoBr_4^{2-} , formed by the analogous reactions (3) and (4). The analogous reaction (5), producing the complex $\text{CoBr}_2(\text{PAH})_2$, is also likely to have occurred since at molar ratios exceeding $2 : 1$ the spectral and elemental analyses revealed the complex CoBr.PAH.PA , where PA denotes the anion of picolinic acid and PAH its undissociated molecule. At a molar ratio of $4 : 1$ all cobalt was in the form of this insoluble complex and the solution was colourless.

The octahedral complexes $\text{CoBr}_2(\text{PAH})_4 \cdot 2\text{HBr}$, which according to Ellis¹⁶ contain tetrahedral species CoBr_4^{2-} and probably even the five-coordinate monomers¹⁷ $\text{CoBr}(\text{PA})(\text{PAH})$, may have been formed too. In an excess of picolinic acid the latter complexes dissolve and the solution exhibits an absorption maximum at 20550 cm^{-1} (Fig. 6, spectrum 3). The absorption is caused by the transition ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$ in the arising octahedral complex $\text{Co}(\text{PA})_2 \cdot 2\text{AcOH}$ or $\text{Co}(\text{PA})_2 \cdot 4\text{AcOH}$. The absorption peaks of complexes $\text{Co}(\text{PA})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{PA})_2 \cdot 4\text{H}_2\text{O}$ were reported¹⁶ to occur at 20200 and 20600 cm^{-1} , respectively. The latter two complexes are formed by reaction of picolinic acid with cobalt dibromide in aqueous media. In non-aqueous media or in acetic acid at a low excess of picolinic acid complexes with contain bromide ligands in their coordination shells are formed.

REFERENCES

1. Gill N. S., Nyholm R. S.: *J. Inorg. Nucl. Chem.* **18**, 88 (1961).
2. Allan J. R., Brown D. H., Nottall R. H., Sharp D. W. A.: *J. Inorg. Nucl. Chem.* **26**, 1895 (1964).
3. Chemische Fabrik Kalk: *Ger.* **2** 103 142 (1972).
4. Hronec M., Pfikryl R., Veselý V.: *Chem. Zvesti* **29**, 440 (1975).
5. Artzukhova E. P., Bulova V. I.: *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* **14**, 1430 (1971).
6. Nelson S. M., Shepard T. M.: *J. Chem. Soc.* **1965**, 3284.
7. King H. C. A., Körös E., Nelson S. M.: *J. Chem. Soc.* **1963**, 5449.
8. Jolley K. W., Buckley P. D., Blackwell L. F.: *Atus. J. Chem.* **25**, 1311 (1975).
9. Arkhpova N. V., Muftakhov A. G.: *Zh. Neorg. Khim.* **16**, 2457 (1971).
10. Artyukhova E. P., Dulova V. I.: *Zh. Fiz. Khim.* **46**, 510 (1972); **47**, 559 (1973).
11. Muftakhov A. G., Reshetnikova R. V., Rakhimov Ch. P.: *Zh. Neorg. Khim.* **18**, 172 (1973).
12. Lever A. B. P., Mantovani E.: *Can. J. Chem.* **51**, 1567, 1973; **51**, 1582 (1973).
13. Cotton F. A., Goodgame D. M. L., Goodgame M.: *J. Amer. Chem. Soc.* **83**, 4690 (1961).
14. Farina R. D., Swinehart J. H.: *Inorg. Chem* **11**, 645 (1972).
15. Proll P. J., Sutcliffe L. H.: *J. Phys. Chem.* **65**, 1993 (1961).
16. Ellis V. M., Vaggr R. S., Watton E. C.: *J. Inorg. Nucl. Chem.* **36**, 1031 (1974).
17. Shaw K. H., Sutton G. J.: *Aust. J. Chem.* **22**, 1835 (1969).

Translated by J. Salák.