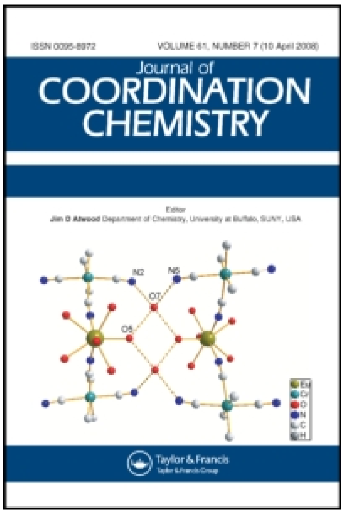

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PREPARATIVE AND ANALYTICAL STUDIES OF SOME DICARBOXYLATO-α-DIIMINECOBALT(III) COMPLEXES*

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Two series of $[Co(III)(AA)_2(OCOR)_2]NO_3$ complexes (where AA = 1,10-phenanthroline or 2,2′-bipyridine and R = H, CH_3, C_2H_5 or C_3H_7) were prepared by the reaction of $[Co(III)(AA)_2CO_3]NO_3$ with the appropriate carboxylic acid in aqueous solution at 50–60°C. A convenient high-yield route to $[Co(phen)_2CO_3]NO_3$ is proposed. The complexes were characterized spectroscopic and by chromatographic (TLC) techniques. A linear relationship is found between the number of carbon atoms in the carboxylic ligand and the chromatographic R_M values of the two homologous series of complexes.

Keywords: Complexes, cobalt(III), diimines, carboxylates, synthesis

INTRODUCTION

The coordination compounds of cobalt(III) with ligands containing nitrogen and oxygen as donor atoms have been the subject of considerable investigations and the greatest interest has been in the complexes with ammonia or ethylenediamine and analogues as nitrogen ligands. Although different and interesting behaviour was observed by substituting these ligands with other nitrogen containing chelate groups, such as *o*-phenanthroline[1–2] or 2,2′-bipyridine,[3–4] cobalt(III) coordination compounds of these types have been dealt with in relatively few papers.[5] As an extension of previous work dealing with the preparation of mixed ethylenediamine-*o*-phenanthroline or 2,2′-bipyridine cobalt(III) nitrato complexes,[6] in this paper the preparation and characterization of mixed cobalt(III) complexes of the type $[Co(AA)_2(OCOR)_2]NO_3$ (AA = 1,10-phenanthroline or 2,2′-bipyridine), where R = H, CH_3, C_2H_5 and C_3H_7, is reported. The compounds to our knowledge have not been previously prepared, except for *cis*-$[Co(bipy)_2(OCOCH_3)_2]^+$, in the perchlorate form.[7] Furthermore, a more convenient high-yield route to $[Co(phen)_2Co_3]NO_3$ is proposed.

EXPERIMENTAL

All solvents and chemicals used were obtained from Merck (Darmstadt, F.R.G.).

Preparation of complexes

Published methods were used to prepare *cis*-$[Co(phen)_2Cl_2]Cl$[8] and *cis*-$[Co(phen)_2(OH_2)_2](NO_3)_3$.[2]

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[Co(phen)$_2$CO$_3$]NO$_3$

5.87 g (0.02 mol) of $Co(NO_3)_2.6H_2O$ and 7.95 g (0.04 mol) of *o*-phenanthroline were nearly completely dissolved in 100 cm^3 of water. 4 cm^3 of 30% H_2O_2 (0.04 mol) were added to the solution dropwise with stirring. To the resulting mixture an aqueous solution of sodium carbonate (5.8 g, 0.02 mol) was added and the mixture evaporated on the steam bath until its volume was reduced to 50 cm^3. During the concentration the colour of the slurry changed very slowly from brown to red as the carbonato complex was formed. The resulting solution was allowed to cool overnight at room temperature, and a red precipitate was obtained. This precipitate was collected in a sintered glass funnel and washed with acetone until the washings were colourless. The solid was then dissolved in the minimum amount of hot water, leaving an insoluble impurity, probably cobalt(III) hydroxide, on the funnel. A small amount of solid $LiNO_3$ was added to the solution, and a red precipitate of [Co(phen)$_2$ CO$_3$]NO$_3$ appeared soon after. The precipitate was filtered and washed with acetone. Yield: 47.5%.

[Co(bipy)$_2$CO$_3$]NO$_3$

This complex was prepared by the same procedure used for the preparation of [Co(phen)$_2$CO$_3$]NO$_3$. Yield: 40%.

(Dicarboxylato)-a-diimine-cobalt(III) nitrate

All the complexes were prepared by a similar procedure of which the following is representative.

[Co(phen)$_2$(OCOH)$_2$]NO$_3$

2.18 g (4 mmol) of [Co(phen)$_2$CO$_3$]NO$_3$ was dissolved in 50 cm^3 of hot water. 2 cm^3 of formic acid (0.06 mol) were added to the solution and the resulting mixture was evaporated on the steam bath to a small volume. The solution was allowed to cool overnight at room temperature and a red-violet crystalline precipitate was obtained. The formate complex was recrystallized from methanol and washed with ether. Yield: 77%.

When $R = CH_3$, C_2H_5 or C_3H_7, the ease of directly obtaining a crystalline product decreases as the length of the carboxylato ligand chain increases. In some experiments, when the reaction mixtures were concentrated on the steam bath, an oil was obtained. Nevertheless a crystalline precipitate was obtained by grinding the oil in a mortar with acetone. The precipitate was dissolved in methanol and an excess of ether was added. A brown precipitate formed immediately, which was filtered off. The solution was evaporated to dryness on the steam bath. A crystalline precipitate was obtained by grinding the residue in a mortar with acetone. The red-violet crystalline precipitate was filtered off and washed with ether. Yields: 35–50%. The attributed formulae and analyses of the prepared compounds are given in Table I. Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer 240 elemental analyser. Cobalt was determined by atomic absorption spectrophotometry (Instrument Laboratory 151).

TABLE I
Elemental analyses for the cobalt(III) complexes.

Complex	Found (Calc.)%			
	Co	C	H	N
$[Co(phen)_2(OCOH)_2]NO_3$	10.2(10.3)	52.9(50.4)	3.2(3.1)	12.5(12.3)
$[Co(phen)_2(OCOCH_3)_2]NO_3$	10.0(9.8)	55.5(56.1)	4.5(3.7)	11.9(11.7)
$[Co(phen)_2(OCOC_2H_5)_2]NO_3$	9.2(9.4)	58.2(57.4)	3.9(4.2)	11.0(11.2)
$[Co(phen)_2(OCOC_3H_7)_2]NO_3$	8.9(9.0)	58.5(58.6)	5.2(4.6)	10.6(10.7)
$[Co(bipy)_2(OCOH)_2]NO_3$	11.6(11.3)	51.4(50.5)	3.0(3.5)	13.6(13.4)
$[Co(bipy)_2(OCOCH_3)_2]NO_3$	10.5(10.7)	52.0(52.3)	4.8(4.0)	12.5(12.7)
$[Co(bipy)_2(OCOC_2H_5)_2]NO_3$	10.1(10.2)	54.5(53.9)	4.4(4.5)	12.1(12.1)
$[Co(bipy)_2(OCOC_3H_7)_2]NO_3$	9.9(9.7)	54.6(55.4)	5.5(5.0)	11.8(11.5)

Characterization of complexes

Electronic spectra were measured using a Perkin-Elmer 559 spectrophotometer. A Perkin-Elmer 298 infrared spectrophotometer was used to obtain spectra in the range between 4000 and 600 cm^{-1}. The samples were prepared as KBr disks.

Thin layer chromatography was performed on HPTLC pre-coated silica gel plates (Kieselgel 60, 5635, Merck) and *n*-alkyl chemically bonded silica gel plates (RP-18, 15683, Merck). The complexes were dissolved in MeOH or in H_2O. Portions (0.5 – 2 μl) of 10^{-3} M solutions of complexes were applied 1 cm from the lower edge of the plates (5 × 5 cm) which were developed in 10–20 min by using as mobile phases DMSO-MeOH-1.3 M $LiNO_3$ in MeOH (3 : 2 : 1) (silica gel plates) or DMSO-H_2O-1.3 M $LiNO_3$ in H_2O (3 : 2 : 1) (RP-18 plates). The spots were visualized with $(NH_4)_2S_x$ and R_f values found are given in Table II.

TABLE II
Spectral and chromatographic data for the cobalt(III) complexes.

Complex	λ^a, nm	ε^b, $M^{-1}\,cm^{-1}$	R_f^c	R_f^d
cis-$[Co(phen)_2(OCOH)_2]NO_3$	510	100.0	0.68	0.54
cis-$[Co(phen)_2(OCOCH_3)_2]NO_3$	509	80.0	0.77	0.37
cis-$[Co(phen)_2(OCOC_2H_5)_2]NO_3$	510	128.6	0.86	0.19
cis-$[Co(phen)_2(OCOC_3H_7)_2]NO_3$	504	104.0	0.94	0.09
cis-$[Co(bipy)_2(OCOH)_2]NO_3$	510	90.5	0.27	0.47
cis-$[Co(bipy)_2(OCOCH_3)_2]NO_3$	510	120.0	0.39	0.35
cis-$[Co(bipy)_2(OCOC_2H_5)_2]NO_3$	509	109.0	0.48	0.20
cis-$[Co(bipy)_2(OCOC_3H_7)_2]NO_3$	505	129.8	0.57	0.00

[a] Wavelengths for absorption maxima. [b] Extinction coefficients at maxima. [c] Retardation factor (silica gel). [d] Retardation factor (C-18).

RESULTS AND DISCUSSION

Preparation and characterization of the complexes

The $[Co(AA)_2(OCOR)_2]^+$ complexes were prepared in the nitrate form and the method for their preparation was based on experiments on the synthesis of the $[Co(phen)_2(OCOH)_2]NO_3$. The progress of the attempted syntheses was followed by TLC; preliminary experiments had shown the possibility of separating the desired complex from its precursor and byproducts.

Various synthetic routes were attempted, differing in the solvent (non aqueous or aqueous), the precursor complex, the nature of the ligand (carboxylic acid or the corresponding anhydride) and temperature (ambient to 60°C). Dimethylsulfoxide and *N,N*-dimethylformamide, the latter being successfully employed for the preparation of other Co(III)-phenanthroline complexes,[6] proved to be satisfactory solvents for the precursor complexes and several syntheses were attempted in these solvent media. As precursor complexes, the $[Co(phen)_2(OH_2)_2](NO_3)_3$ or the corresponding carbonate were employed. In particular, for the $[Co(phen)_2CO_3]NO_3$ complex a different synthesis was developed. A three step process has been reported in the literature:[9] $Co(II) \rightarrow [Co(phen)_2Cl_2]Cl \rightarrow [Co(phen)_2(OH_2)_2](NO_3)_3 \rightarrow [Co(phen)_2CO_3]NO_3$. The yield, in our hands, was not satisfactory (10% of purified $[Co(phen)_2CO_3]NO_3$ based on cobalt(II)). Otherwise, the one step synthesis as described above was found to be reliable, and it is to be recommended for its simplicity and reliably high yield (47%).

Preliminary experiments have shown that anation of the diaquo complex is unsuitable, whereas the substitution of the carbonato ligand gives good results. Thus the method chosen for the preparation of the dicarboxylato nitrates involved reaction of $[Co(phen)_2CO_3]NO_3$ or $[Co(bipy)_2CO_3]NO_3$ with the appropriate carboxylic acid in water at about 50°C. In the case of the diformato complexes, a crystalline chromatographically pure compound with high yield (75%) was easily obtained. In the other syntheses, lower yields were found (35–50%), as successive purifications proved to be necessary.

With respect to the solubility of the prepared complexes, methanol, water and DMSO are better solvents than ethanol. The diformate complexes are the least soluble of all compounds examined. These phenanthroline and bipyridine complexes seem to be more inert than the corresponding series of ethylenediamine analogues which, as reported by Haim,[9] easily hydrolyze. Aqueous solutions of the complexes remain unchanged over 24 hrs at 25°C, as revealed by spectral measurements.

From elemental analyses (Table I) the compounds closely correspond to the formula $[Co(AA)_2(OCOR)_2]NO_3$. The I.R. spectra of the four complexes of each series are very similar. The spectra show the presence of non-coordinated nitrate ion (characteristic band at 1390 cm^{-1}) and confirm the coordination of carboxylate ligands. The presence of two very intense bands near 1635 and 1340 cm^{-1} indicate that the carboxylate groups are employed in metal ion complexation. The bands due to the *N*-ligands in the complexes were identified by comparison with the spectrum of free phenanthroline or free bipyridine. As expected (from literature data) when phenanthroline is coordinated to the cobalt ion, bands in the region of 700–800, 1400 and 1500 cm^{-1} are slightly displaced; in our case to 850–860, 1430 and 1525 cm^{-1}, respectively. The shifts observed compare well with data reported for other mixed *bis*-phenanthroline cobalt(III) complexes.[11] In the case of the bipyridine complexes, slight shifts with respect to the free ligand are also observed. The configuration of the complexes may be assigned on the basis of the visible spectrum. Spectral data are listed in Table II. All the spectra are similar to those of *cis*-compounds of similar series. Many authors[2,7,11] have commented that the existence of *trans*-isomers has never been verified and the early report of *trans*-$[Co(bipy)_2Cl_2]^+$ by Jaeger and Van Dijk[3] has been disproven.[12]

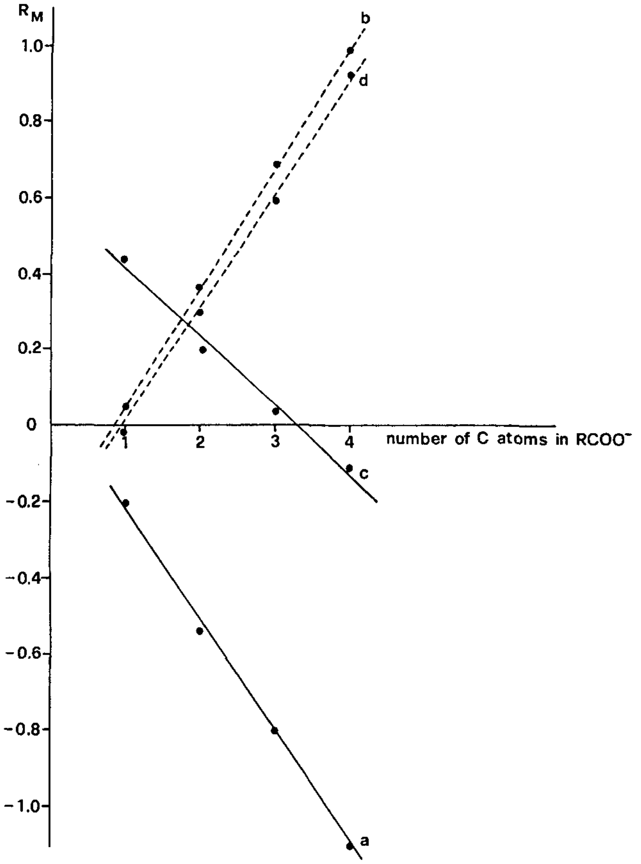

FIGURE 1 Retention of *cis*-$[Co(phen)_2(OCOR)_2]NO_3$ (a, b) and *cis*-$[Co(bipy)_2(OCOR)_2]NO_3$ (c, d) as a function of the number of carbon atoms in the carboxylato ligands over silica gel (—) and RP-18 (- - -) thin layers. Eluents: (—) DMSO-MeOH-1,3 M $LiNO_3$ in MeOH (3 : 2 : 1); (- - -) DMSO-H_2O-1,3 M $LiNO_3$ in H_2O (3 : 2 : 1).

Structure–chromatographic retention correlation

In Fig. 1 the correlation between the R_M values of both series of complexes and the number of carbon atoms in the carboxylato ligands is shown. This correlation can be used for a structure–chromatographic retention investigation.[13] The R_M values were calculated on the basis of the measured R_f values (see Table II) by the well-known equation $R_M = \log(1/R_f - 1)$. The reported relationships are linear both on silica gel and on RP-18 layers. In the first case, a decrease in retention with increasing carbon atom number was noted and the solubilities of complexes in DMSO parallel their R_f values. On RP-18 layers, as expected, a corresponding reversal in retention order was found. This difference between the two chromatographic systems can be explained on the basis of different mechanisms of retention. On silica gel many effects are possible, the stronger being, probably, the steric hindrance of adsorption. In the case of RP-18 layers, where the retention behaviour is governed by hydrophobic interactions, the extent of the retention is a function of the alkyl chain-length of the complexes; the di-*n*-butyrato complexes show the lowest mobility. Moreover, the observed linear relationships suggest that the prepared complexes are members of two homologous series, as linear plots of the logarithmic retention factor (R_M) *versus* the number of carbon atoms in the alkyl substituents have been obtained.[14,15]

The above correlations confirm that the prepared complexes have the same structure and that aquation products, probably formed during their syntheses, do not effect the final species isolated.

REFERENCES

1. P. Pfeiffer and B. Werdelmann, *Z. Anorg. Allgem. Chem.*, **263**, 31 (1950).
2. A.V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).
3. F.M. Jaeger and J.A. Van Dijk, *Z. Anorg. Allgem. Chem.*, **227**, 273 (1936).
4. D.M. Palade, A.V. Ablov and V.N. Zubarev, *Russ. J. Inorg. Chem.*, **14**, 227 (1969).
5. R.W. Hay, *Coord. Chem. Rev.*, **71**, 37 (1986).
6. G. Grassini-Strazza, M. Sinibaldi and A. Messina, *Inorg. Chim. Acta*, **44**, L295 (1980).
7. F. Aprile and F. Maspero, *Atti Accad. Naz. Lincei, Classe Sci. Fis., Mat. e Nat., Rend.*, **39**, 310 (1965).
8. G. Grassini-Strazza and S. Isola, *J. Chromatogr.*, **154**, 127 (1978).
9. A.V. Ablov and D.M. Palade, *Russ. J. Inorg. Chem.*, **6**, 306 (1961).
10. T.J. Przystas, J.R. Ward and A. Haim, *Inorg. Chem.*, **12**, 743 (1973).
11. D.M. Palade, Yu.L. Popov and E.S. Il'ina, *Russ. J. Inorg. Chem.*, **17**, 228 (1972).
12. F. Aprile, M. Lederer and F. Maspero, *Atti Accad. Naz. Lincei, Classe Sci. Fis., Mat. e Nat., Rend.*, **36**, 70 (1964).
13. B.K. Chen and C. Horvath, *J. Chromatogr.*, **171** 15 (1979).
14. M. Bidlo-Igloy, F. Szederkenyi and E. Tihanyi, *J. Chromatogr.*, **361**, 145 (1986).
15. G. Vuckovic, N. Juranic and M.B. Celap, *J. Chromatogr.*, **361** 217 (1986).