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Reactions of CrO_2Cl_2, $FeCl_2$, $FeCl_3$, $CoCl_2$, $MoCl_5$ and $AlCl_3$ with Benzofuroxan. II.

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Abstract

By reaction of benzofuroxan ($B = C_6H_4N_2O_2$) with CrO_2Cl_2, $FeCl_2$ and $AlCl_3$ the compounds $CrO_2Cl_2 \cdot B$, $FeCl_2 \cdot B$ and $AlCl_3 \cdot B$ were obtained. With $FeCl_3$ the compound $[FeCl_2B_2]^+[FeCl_4]^-$ was obtained and the reaction with $CoCl_2$ leads to the compound $CoCl_2 \cdot 2B$. The reaction with $MoCl_5$ takes place with reduction of this compound and the isolation of $MoCl_4 \cdot 2B$.

The reactions of the ligand with anhydrous $MnCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ were also studied but they always took place with negative results.

The compounds were characterized by elementary analysis, conductivity measurements and IR, UV–Vis and EPR spectroscopy.

Introduction

As a continuation of the study of the reactivity of benzofuroxan with covalent anhydrous metallic halides [1–3], we present in this paper the investigated reactions with CrO_2Cl_2, $FeCl_2$, $FeCl_3$, $CoCl_2$, $MoCl_5$ and $AlCl_3$. We used $AlCl_3$ in order to try to observe the presence of species like $AlCl_4^-$ as was the case in the reaction with $FeCl_3$.

Results and Discussion

As repeated attempts to obtain defined compounds in the reaction between $CrCl_3$ and benzofuroxan failed, we used a more reactive chromium compound like CrO_2Cl_2. The reaction between this compound and benzofuroxan leads to the formation of the complex $CrO_2Cl_2 \cdot 2C_6H_4N_2O_2$; it was studied by IR spectroscopy and the main bands of the spectrum are given in Table I. These bands correspond to the asymmetric and symmetric stretching bands of the Cr–Cl and Cr–O coordinated bonds. Furthermore, two bands at 958 and 932 cm^{-1} appear, which can be assigned to the asymmetric and symmetric stretching vibrations of the Cr=O bonds; this means that after the coordination, the frequency of vibrations of the CrO_2Cl_2 decreases, which was logically expected [4].

TABLE I. IR Spectra of Complexes[a]

Compound	ν(M–O)	ν(M–Cl)$_t$	ν(M–Cl)$_{bridge}$
$CrO_2Cl_2 \cdot C_6H_4N_2O_2$	429m	394m,s 372s	
$FeCl_3 \cdot C_6H_4N_2O_2$	459m	380s,b	
$FeCl_2 \cdot C_6H_4N_2O_2$	463m	303s	241m 232m
$CoCl_2 \cdot 2C_6H_4N_2O_2$	377s	340s 330sh	
$MoCl_4 \cdot 2C_6H_4N_2O_2$	420m 385m,s	360s 330vs 310sh 290w	

[a] In cm^{-1}. s = strong; m = medium; w = weak; sh = shoulder; b = broad.

In relation to the compounds, with $FeCl_3 \cdot C_6H_4N_2O_2$ stoichiometry, obtained by the reaction between $FeCl_3$ and benzofuroxan, the conductivity measurements in nitrobenzene solutions indicate that they are 1:1 electrolytes and for that reason we propose the following structure $[FeCl_2B_2]^+[FeCl_4]^-$ for the compound. This formula is also supported by the IR spectroscopic data. In the low frequency range, the IR spectrum presents one strong and broad band at 380 cm^{-1}, which is assigned to the ν_3 active mode of the tetrachloroferrate(III) tetrahedral anion, in agreement with other data found in the bibliography [5, 6]. This broad band, which also has several shoulders, probably masks the one which corresponds to the stretching vibration of the Fe–Cl bond in the complex cation $[FeCl_2B_2]^+$. These bands and also the one corresponding to the stretching vibration of the Fe–O bond are given in Table I.

In the electronic spectrum in CH_2Cl_2 solution, the d–d observed bands are weak and broad as expected

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for these types of transitions [7, 8]. These bands are observed at 19 000 and 14 900 cm^{-1}, which are very near to those of the tetrachloroferrate ions [7].

In the UV spectrum two bands are observed at 31 700 and 27 400 cm^{-1}, which are also characteristic of $[FeCl_4]^-$ [7, 9].

In the EPR complex, recorded at room temperature, either in CH_2Cl_2 solution or as a suspension in KBr, one single isotropic signal is obtained, for which a value of $g_{iso} = 2.01$ is calculated and a linewidth of 130 gauss. This value is comparable with those obtained for other complexes in which the presence of $[FeCl_4]^-$ is implied [8, 10, 11]. No hyperfine coupling in Fe(III) is observed, because with the low natural abundance of ^{57}Fe it is very difficult to detect, except if the metal is enriched with the magnetic isotope [12].

The reaction between $FeCl_2$ and benzofuroxan leads to the formation of the compound $FeCl_2 \cdot C_6H_4N_2O_2$. The molar conductivity data indicate that it is not an electrolyte.

Some studies made with iron(II) complexes of the type FeX_2L_n, indicate that there is a strong tendency for hexacoordinated species to form polymeric structures with halogen bridges [13, 14]. In other compounds, obtained by iron carbonyls and other ligands (benzamide, aniline) [15], the existence of dimers with halogen bridges, in which the Fe(II) is tetracoordinated, has been suggested.

As in the IR spectrum of our compound (Table I) it is possible to observe clear bands which correspond to the ν(Fe–Cl)(terminal), ν(Fe–Cl)(bridge) and ν(Fe–O) stretching vibrations, we propose a polymeric structure for it, with chloro bridges between the iron atoms which will be hexacoordinatively surrounded.

The compound $CoCl_2 \cdot 2C_6H_4N_2O_2$ is obtained from the reaction between anhydrous $CoCl_2$ and benzofuroxan using chloroform as solvent. The IR spectrum of the compound (Table I) allows us to observe that the ν(Co–Cl) frequencies are in agreement with those described in the literature for tetrahedral Co(II) species [16].

The visible spectrum, in ethanol solution, presents one band with multiple absorption (17 200, 16 100, 14 900 cm^{-1}) which is also characteristic of the tetrahedral Co(II) species and which corresponds to the $^4T_1(P) \leftarrow {}^4A_2$ transition [7, 17].

We also registered the EPR spectrum in ethanol solution at −160 °C. Theoretically, the hyperfine coupling in ^{59}Co has a value about twice or three times greater in an octahedral than in a tetrahedral crystal field, which is based on the A values obtained by the equations described in the bibliography [12]. In our case, we obtained only one single signal in the spectrum, and a value of $g_{iso} = 2.008$ with a linewidth of 45 gauss can be deduced from it; because of the small coupling and the big width of the line, the eight signals expected for an hyperfine coupling were not observed. This fact has been also considered in other Co(II) complexes with Schiff bases as ligands [18, 19].

In the reaction of $MoCl_5$ with benzofuroxan, a reduction to the Mo(IV) complex, $MoCl_4 \cdot 2C_6H_4N_2O_2$, took place. In fact, the reduction of the molybdenum pentachloride in the presence of donor molecules, is one of the more common synthesis procedures followed for the preparation of neutral coordination compounds of molybdenum tetrachloride [20].

The experimental data indicate that the compound $MoCl_4 \cdot 2C_6H_4N_2O_2$ is an octahedral monomer in which the ligand molecules are placed in the *cis* position. In the IR spectrum, the absence of one strong band around 1000 cm^{-1} (ν(Mo=O)) indicates that the compound has no oxomolybdenum impurities.

The modes which correspond to the Mo–Cl stretching vibrations (Table I) are in the range of the characteristic frequencies of octahedral Mo(IV) species [5]. This assignment suggests that the ligands are in *cis* positions, because if placed in a *trans* position only one band for the metal–chloro and metal–ligand stretching vibrations should be expected.

The visible spectrum, recorded in CH_2Cl_2 solution, is analogous to those obtained for other hexacoordinated Mo(IV) species [7, 21, 22]. In an octahedral environment, the fundamental term is $^3T_{1g}$, and for that reason the intense band at 17 500 cm^{-1} and the shoulder at 24 000 cm^{-1} can be assigned to the $^3T_{2g} \leftarrow {}^3T_{1g}$ and $^3T_{1g}(P) \leftarrow {}^3T_{1g}$ transitions, followed by another one at 26 700 cm^{-1} that probably is due to a charge transfer.

In the reaction of $AlCl_3$ with benzofuroxan, a compound with $AlCl_3 \cdot C_6H_4N_2O_2$ stoichiometry is isolated. The structure of the 1:1 complexes of $AlCl_3$ with organic ligands is generally covalent with a tetrahedral coordination around the metal [23–25]; however, in other cases, ionic structures are considered, because it is possible to formulate 1:1 complexes which contain the tetrahalide ion, as in the case of the $[AlX_2L_2]^+[AlX_4]^-$ species. For our compound, the conductivity values measured in nitrobenzene solution, indicate with absolute security that the structure is covalent.

If we examine the IR spectrum of the complex we can see some broad and intense bands below 550 cm^{-1}, that can be assigned to skeleton vibration modes and are characteristic of aluminium halides complexes. Of the six vibration modes of the metal–halide skeleton, which should be expected in the spectrum, only the ν_1 (387 cm^{-1}, A_1), the ν_2 (482 cm^{-1}, A_1) and the ν_4 (543 cm^{-1}, E) are observed, considering a C_{3v} local symmetry around the aluminium atom [24, 26]. The band which appears at 587 cm^{-1} is assigned to the ν(Al–O) vibration.

TABLE II. Analytical Data[a] and Melting Points for the Compounds

Compound	%C	%N	Metal	%Cl	Melting point (°C)
$CrO_2Cl_2 \cdot C_6H_4N_2O_2$	24.29(24.75)	9.64(9.62)	17.46(17.87)	22.88(24.37)	165 dec.
$FeCl_3 \cdot C_6H_4N_2O_2$	25.07(24.14)	9.26(9.38)	18.64(18.72)	34.54(35.66)	183 dec.
$FeCl_2 \cdot C_6H_4N_2O_2$	25.80(27.42)	9.86(10.65)	21.09(21.25)	25.73(26.98)	190 dec.
$CoCl_2 \cdot 2C_6H_4N_2O_2$	37.76(35.86)	13.04(13.93)	14.20(14.66)	18.55(17.64)	220 dec.
$MoCl_4 \cdot 2C_6H_4N_2O_2$	27.62(28.27)	10.92(10.98)	17.78(18.82)	29.44(27.81)	180 dec.
$AlCl_3 \cdot C_6H_4N_2O_2$	26.64(26.75)	9.94(10.39)	9.81(10.01)	38.08(39.48)	64 dec.

[a]% Found (calculated).

Experimental

All reactions and manipulations were carried out under anhydrous conditions (dry N_2, glove box) because all the compounds are very sensitive to hydrolysis. Analytical data and melting points for the compounds are given in Table II.

$CrO_2Cl_2 \cdot C_6H_4N_2O_2$

A solution of 1.92 g (12.4 mmol) of CrO_2Cl_2 [27] in CH_2Cl_2 in a dropped funnel was added under magnetic stirring to a double necked flask containing a solution of 3.37 g (24.8 mmol) of $C_6H_4N_2O_2$ in CH_2Cl_2 at room temperature. The reaction was lightly exothermic and after 4 h the solution was filtered off, with a glass-frite under dry N_2, and the resultant dark brown solid washed with dry CH_2Cl_2 and dried in vacuum.

$FeCl_3 \cdot C_6H_4N_2O_2$

A solution of 2.64 g (19.4 mmol) of $C_6H_4N_2O_2$ in $CHCl_3$ was added under magnetic stirring to a solution of 0.70 g (4.3 mmol) of $FeCl_3$ also in $CHCl_3$ at room temperature. Afterwards, the mixture was kept under reflux for about 15 h. A very dark (almost black) solid was separated, which was filtered off, washed with $CHCl_3$ and dried in vacuum.

The molar conductivity measurements, made in 0.1 M nitrobenzene solution, gave the following value $\Lambda_M = 29.8$ ohm^{-1} cm^2 mol^{-1}.

$FeCl_2 \cdot C_6H_4N_2O_2$

In this case, special care was taken to avoid the presence of oxygen in the reaction vessel. To a suspension of 0.5 g (4 mmol) of $FeCl_2$ [28] in CH_2Cl_2, a solution of 2.18 g (16 mmol) of $C_6H_4N_2O_2$ in CH_2Cl_2 was added under magnetic stirring at room temperature. After 4 days of stirring in the same conditions, a dark brown solid appeared, which was filtered off, washed with CH_2Cl_2, and dried in vacuum. $\Lambda_M = 9.13$ ohm^{-1} cm^2 mol^{-1} for a 10^{-3} M solution in nitrobenzene.

$CoCl_2 \cdot 2C_6H_4N_2O_2$

A solution of 4.11 g (30.2 mmol) of $C_6H_4N_2O_2$ in $CHCl_3$ was added under magnetic stirring at room temperature, to a suspension of 0.82 g (6.3 mmol) of $CoCl_2$ in $CHCl_3$. The magnetic stirring was continued at room temperature for 40 h and afterwards the dark brown solid obtained was filtered off, washed with $CHCl_3$ and dried in vacuum.

$MoCl_4 \cdot 2C_6H_4N_2O_2$

A solution of 1.7 g (12.5 mmol) of $C_6H_4N_2O_2$ in CH_2Cl_2 was added with magnetic stirring at room temperature to a suspension of 2.25 g (8.2 mmol) of $MoCl_5$ and afterwards the mixture was heated to reflux for 20 h. During the reaction an evolution of chlorine gas was observed and checked (with fluoresceine and KBr). After 20 h a red–brown solid was obtained which was filtered off, washed with CH_2Cl_2 and dried in vacuum.

$AlCl_3 \cdot C_6H_4N_2O_2$

A solution of 2.17 g (16 mmol) of $C_6H_4N_2O_2$ in CH_2Cl_2 was added with magnetic stirring at room temperature to a suspension of 2.13 g (16 mmol) of $AlCl_3$ in CH_2Cl_2 resulting in a clear brown solution. Part of the solvent was eliminated under vacuum and some cyclohexane was added to give a dark brown oil; under strong vacuum a beige solid could be isolated from this oil.

The $AlCl_3$ was purified in vacuum under the action of a mixture of dry NaCl and a small amount of Al metal. The CH_2Cl_2 used was previously 'immunized' by treatment under reflux with an excess of $AlCl_3$ [23]. $\Lambda_M = 1.35$ ohm^{-1} cm^2 mol^{-1} (in 10^{-3} M nitrobenzene solution).

The IR spectra were recorded on a Nicolet 5DX spectrophotometer in the range 5000–200 cm^{-1}, using Nujol and hexachlorobutadiene, with CsI windows.

The electronic spectra were recorded on a Pye Unicam SP8-100 spectrophotometer, using quartz-glasses of 1 cm thickness.

The molar conductivity measurements were made on a Methrom Herisau E-518 conductimeter.

The EPR spectra were recorded on a Varian E-12 spectrophotometer at a microwave frequency of 9 GHz (X-band), equipped with a HP 5342 A frequency meter and a Bruker NMR Gaussmeter. The samples were introduced into quartz-glasses of 4 mm diameter. The low temperature spectra were obtained using a variable temperature cell.

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References

1 V. Fernández and C. Muro, *Z. Anorg. Allg. Chem., 466,* 209 (1980).

2 D. Tudela, C. Muro, V. Fernández and J. D. Tornero, *Z. Anorg. Allg. Chem., 538,* 201 (1986).

3 C. Muro and V. Fernández, *Inorg. Chim. Acta,* submitted for publication.

4 R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals', Wiley-Interscience, New York, 1969.

5 J. R. Ferraro, 'Low-Frequency Vibrations of Inorganic and Coordination Compounds', Plenum, New York, 1971.

6 U. Demant, E. Conradi, J. Pebler, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem., 515,* 69 (1984).

7 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', 2nd edn., Elsevier, Amsterdam, 1984.

8 S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A,* 859 (1971).

9 R. J. Woodruff, J. L. Marini and J. P. Fackler, *Inorg. Chem., 3,* 687 (1964).

10 S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A,* 2105 (1970).

11 S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A,* 1690 (1971).

12 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem., 13,* 135 (1970).

13 T. Birchall and M. F. Morris, *Can. J. Chem., 50,* 201 (1972).

14 D. M. L. Goodgame, M. Goodgame, M. A. Hitchman and M. J. Weeks, *Inorg. Chem.,* 635 (1966).

15 T. Birchall, *Can. J. Chem., 47,* 1351 (1969).

16 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chim. Acta, 26,* 57 (1978).

17 E. R. Menzel, W. R. Vincent, D. K. Johnson, G. L. Seebach and J. R. Wasson, *Inorg. Chem., 13,* 2465 (1974).

18 G. Labauze and J. B. Raynor, *J. Chem. Soc., Dalton Trans.,* 2388 (1980).

19 G. Labauze and J. B. Raynor, *J. Chem. Soc., Dalton Trans.,* 590 (1981).

20 W. H. Carmichael and D. A. Edwards, *J. Inorg. Nucl. Chem., 34,* 1181 (1972).

21 E. A. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.,* 1636 (1965).

22 W. H. Carmichael, D. A. Edwards and R. A. Walton, *J. Chem. Soc. A, 97* (1966).

23 D. E. H. Jones and J. L. Wood, *J. Chem. Soc. A,* 1448 (1966).

24 D. H. Brown, D. T. Stewart and D. E. H. Jones, *Spectrochim. Acta, Part A, 29,* 213 (1973).

25 D. E. H. Jones and J. L. Wood, *J. Chem. Soc. A,* 3132 (1971).

26 J. Lewis, J. R. Miller, R. L. Richards and A. Thompson, *J. Chem. Soc.,* 5850 (1965).

27 G. C. Schlessinger, 'Preparación de Compuestos Inorgánicos en el Laboratorio', Editorial Continental, Mexico, 1965.

28 P. Kovacic and N. O. Brace, *Inorg. Synth., 6,* 172 (1960).