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Complexes of Brucine with Pd(II), Cu(II), Co(II) and Ni(II) Chlorides

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Brucine forms complexes with Pd(II), Cu(II), Co(II) and Ni(II) chlorides. Comparison of the IR spectrum of brucine with the spectra of the complexes implies that the transition metals prefer to form complexes with oxygen, except (partially) for nickel, or with the π-electron cloud of the double bond in the case of palladium. The visible-UV spectra, magnetic moments and ESR spectra of the complexes are also reported and discussed.

Introduction

Brucine is a methoxy-derivative of the highly poisonous compound strychnine, and may be recovered along with the latter from the seeds of *Strychnos nux-romira*, a plant of East India. Though not so toxic as strychnine, brucine acts specifically on the spinal cord and on medulla oblongata, stimulating the vasomotive centers [1]. Brucine belongs to the wide family of alkaloids and as far as we know not many alkaloid complexes are reported in the literature, except for a few of quinine with Cu(II), Ni(II), Co(II) and Cr(III) [2].

Brucine is used in analytical chemistry for the determination of NO_2, Cd, Ce, V and certain other entities, without isolating the precipitates. It is also used in the chemistry of natural materials for the resolution of racemic mixtures [3]. Anyway, nothing is mentioned in the literature about the reaction of brucine with Pd^{+2}, Cu^{+2}, Ni^{+2} and Co^{+2}.

Brucine has two nitrogen atoms in a 5-membered and a 6-membered ring, respectively, an O as heteroatom in a 7-membered ring and a double bond. Based on the properties deduced from the chemical formula, we describe in this paper the preparation and the study of the structure of brucine complexes with Cu^{+2}, Pd^{+2}, Co^{+2} and Ni^{+2}, in an attempt to find new compounds with differing .physical or physiological properties.

The structure of the complexes has been studied by IR, ESR and NMR spectroscopy (this latter only for Pd-complexes) as well as by elemental analysis.

Experimental

Brucine was purchased form the Aldrich Company (grade puriss), and the metal salts from Merck (pro analysi). IR spectra were taken with a Perkin-Elmer 283 instrument, ESR spectra with a Varian E-4 instrument (in the solid state), while ^{13}C-NMR spectra were taken with a Varian FT-80A and the UV-VIS spectra with Zeiss Ikon model RP 020 A.

Brucine–PdCl$_2$ Complex, [(brucine)·PdCl]/2

0.01 mol of brucine dihydrate (4.30 g), dissolved in 50 ml of pure ethanol and 50 ml of an aqueous solution of 0.01 *M* (1.77 g) of palladous chloride dissolved with the aid of the corresponding quantity of NaCl and a few drops of hydrochloric acid, were added dropwise under stirring. The solution was stirred for 1 h at 60 °C and an orange precipitate was finally formed which was recovered by filtration, washed with ethanol/water, and dried under vacuum over P_2O_5 for two days. The product decomposes at 255 °C. Yield 72% of the theoretical. *Anal.* Calcd.: C, 51.5; H, 4.84; N, 5.22; Cl, 6.62; Pd, 19.78. Found: C, 50.2; H, 4.3; N, 5.83; Cl, 5.50; Pd, 19.00%.

Brucine–CuCl$_2$ Complex (Brucine)$_2$·CuCl$_2$

0.005 mol (2.15 g) of brucine dihydrate were dissolved in 50 ml of absolute ethanol and 0.0025 mol (0.335 g) of anhydrous $CuCl_2$ added under stirring. The mixture was then stirred for 15 min in the absence of moisture. A red precipitate was formed and immediately filtered, washed with anhydrous ethanol and vacuum dried for 2 days over P_2O_5. The product decomposes at 172–5 °C. Yield 70%. *Anal.* Calcd.: C, 59.8; H, 5.6; N, 6.06; Cl, 7.69; Cu, 6.88. Found: C, 58.8; H, 5.3; N, 5.75; Cl, 6.82; Cu, 7.22%.

Brucine–NiCl$_2$ Complex (Brucine)$_2$·NiCl$_2$

0.005 mol (2.15 g) of brucine dihydrate were dissolved in 50 ml of ethanol and 0.005 mol (1.19 g) $NiCl_2 \cdot 6H_2O$ added under stirring and heating to boiling. The mixture was then stirred under heating for 4 hours. At light yellow-green precipitate was formed, which was filtered and washed with ether/

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alcohol (1:1). The whole was dried in vacuum overnight above P_2O_5. The product decomposes at >330 °C. Yield 63%. *Anal.* Calcd.: C, 60.1; H, 5.66; N, 6.10; Cl, 7.73; Ni, 6.39. Found: C, 59.2; H, 5.4; N, 6.0; Cl, 7.65; Ni, 6.02%.

Brucine–$CoCl_2$ Complex ((Brucine)$_2$·$CoCl_2$)·$2H_2O$

0.005 mol (2.15 g) of brucine dihydrate were dissolved in 50 ml of ethanol and 0.0025 mol (0.555 g) of $CoCl_2·6H_2O$ added under stirring and heating at 50 °C. The mixture was then stirred for 2 hours at the above mentioned temperature, and finally a blue precipitate was formed which was filtered, washed with ether and vacuum dried overnight above P_2O_5. The product decomposes at 285–9 °C. Yield: 79%. *Anal.* Calcd.: C, 57.8; H, 5.86; N, 5.86; Cl, 7.44; Co, 6.17. Found: C, 57.0; H, 5.22; N, 5.80; Cl, 7.30; Co, 6.38%.

Results and Discussion

The IR spectra of brucine with metal chlorides are interpreted in comparison with the IR spectrum of brucine. In this spectrum typical are the vibrations of methyl groups as well as those of the double bond between carbon atoms at the 21- and 22- position, according to the formula proposed by Robinson and Woodward (Fig. 1) [4].

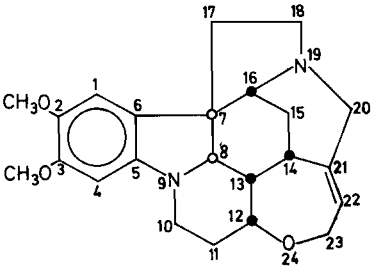

Fig. 1. Structure of brucine.

The vibrations of brucine and its metal chloride complexes being prepared are given in Table I, Fig. 1.

As deduced from the IR spectra, the formation of a π-allylic complex in the brucine–$PdCl_2$ complex molecule with the complexation taking place at the double bond between the two carbon atoms at the 21- and 22- positions is obvious, and the band at 420 cm^{-1} is typical for complexes of this form [5]. A shift of the double bond at the 1520–1400 cm^{-1} is also observed [6]. At 432 cm^{-1} the Pd–C appears, while the Pd–Cl–Pd bridging appears as strong and moderate strong vibrations at 314 and 270 cm^{-1} respectively.

The complexation in form of a π-allylic complex is supported and proved by ^{13}C-NMR spectroscopy. For example a shift toward low field of the carbon atoms at positions 20 and 21 is observed (Fig. 2). This happens because of the de-shielding due to the metal. On the other hand the chemical shift of carbon atoms in the brucine spectrum [7] and in the complex show a difference in the carbon atoms at the above mentioned positions only. The differences between the ^{1}H-NMR spectra of the complex and brucine were not significant, which leads us to conclude that the coordination of Pd^{+2} with nitrogen or oxygen is unlikely to happen. The formation of such a π-complex presents an interest in the synthetic field, because it is possible to prepare brucine derivatives by the action of several nucleophilic compounds [8]. On the basis of these data the possible formula of the complex is ((Bruc)·PdCl)/2.

In the IR spectrum of brucine–$CuCl_2$ complex a shift of the ν(C=O) absorption band by 80 cm^{-1} is observed; this means that it appears at 1655 cm^{-1} instead of the 1685 cm^{-1} of brucine, with further disappearance of the C–O vibration at 1000 cm^{-1}. The peak at 479 cm^{-1} belongs to the ν(Cu–O) vibration while the 240.3 cm^{-1} vibration which belongs to ν(Cu–Cl) also appears. These vibrations are in accordance with the data given in the literature [9]. The observed shift of the carbonyl band is likely to be due to a coordination of copper with the oxygen atom of the carbonyl group. This may also be supported by the appearance of ν(Cu–O) vibrations. There are several vibrations for the ligand appearing in the region 400–300 cm^{-1} corresponding to C–H and C–N vibrations, so that we cannot speak with certainty about the C–N coordination. Anyway the Cu–O coordination is more explicit, as mentioned above. Moreover the double peak of the δ(C–O–C) vibration of brucine disappears after complexation, with only one strong vibration at 1103 cm^{-1} being observed. From this we can presume that Cu^{+2} has one more coordination with the oxygen atom at 24-position (Fig. 1).

The observed ESR spectra of the yellow coloured complex obtained in powder form show that this is rhombically compressed in the fundamental d_{z^2} electronic state [9a]. The parameters are $g_{/\!/} = 2.148$ and $g_{\perp} = 2.035$. We must consider that there is mutual dependence between structure and colour of the copper complexes, in which the complex has a yellow color and all the data are in accordance with those in the literature [10] (Fig. 3).

From the previous data we conclude that the possible formula of the complex is $(Bruc)_2·CuCl_2$.

In the case of brucine complexation with Co^{+2}, an explicit shift of the carbonyl band by 35 cm^{-1} lower than that of the free ligand is observed. Moreover, the C–O–C vibration band of the free ligand which is shown as a strong double peak vibration at 1130 and 1020 cm^{-1} due to assymmetric and symmetric stretching respectively is shifted after complexation by *ca.* 120 cm^{-1} appearing at 1008 and 920 cm^{-1}; of these two the former appears

TABLE I. Frequencies (cm^{-1}) of Brucine Dihydrate and its Complexes with Transition Metal Chlorides.

Brucine	Bruc• PdCl/2	(Bruc)$_2$-CuCl$_2$	(Bruc)$_2$-NiCl$_2$	(Bruc)$_2$•CoCl$_2$•2H$_2$O
	3636s	3600sh		
	3515s	3550s		
		3400sh	3362vs	
		3130s		
		3020		
2920s	2976vs	2950sh		
2895s	2840vs			
	2712vs			
1685vs	1662vs	1655vs	1647vs	1660s
	1616s			1635s
1532s	1499vs	1507vs	1502vs	1505s
1495s				
1480s				1475sh
1445s	1458vs	1460s	1452s	1465s
1432s		1430s		
1410s	1410vs		1415s	1419s
				1405m
1387s				
1350s	1340s			
1328s				
1315s	1312s	1305sh		1315m
1300sh	1289vs	1293s	1287s	1293m
1275	1265s			
1255sh				
1240s	1238vs			
1220s	1215vs		1218s	
1210s	1198vs	1205s	1201s	
		1189s		1190vs
1155s				1160s
1135w	1133vs			
1123w				
1110s	1110vs	1103vs	1114s	1100vs
1090s	1084s	1078m	1085m	1075s
1050s	1050s	1045m	1051m	1045vs
1025s	1036s	1025m	1035m	1025s
1012s	1019s			
	1005s	1003m	1009m	1005m
	983s	982w	987w	990w
				977s
960m	963m	960w		960w
940m				928w
915w	920w	920w		915w
	893w			892w
875vs	885w			880w
867vs	863s			865m
855sh				
840m	844s	847m	846m	847s
815s		819		832m
780s	784m	785m		785w
762w	763s	763w		761m
739m	746s			745w
718w	707w			722w
700w				702w
690w			689vs	
679w	678w			680w
661w				661w
640w	644w	650w		647w
		625w		621w
	613w			613w
587m	595w	590w		
580m		575w		
559m	551m	555m		555m
543m				545sh
		525		525w
				513w
490m				496w
473m		479		465w
	463m		458vs	
455m				
445m				440w
	432m			435w
		418m		
	395w	395m		
	374w		374vs	
		349		
	314vs			
	270s			
		240m	240vs	

TABLE II. UV–VIS Spectra and Effective Magnetic Moments of the Brucine Transition Metal Chloride Complexes.

Complex	λmax in nm	μ_{eff}BM) at 20 °C	
		Calc.	Found
(a)			
(b)	724, 789	1.95	1.73
(c)	725, 659	2.80	2.86
(d)	517	1.70	1.70

moderately strong and the other as a weak double peak band. These results are in accordance with the literature [11]. The bands of the IR spectrum appearing at 555 and 440 cm^{-1} of the complex are attributed to the ν(Co–O) vibrations [12]. We therefore conclude that the possible coordination of Co^{+2} takes place with the carbonyl oxygen and with the oxygen atom at the 24-position of the molecule (Fig. 1).

By the ESR spectrum of the complex its paramagneticity is ascertained. The parameters of the spectrum are: $g\perp = 2.0285$ and $g/\!/ = 2.1832$ (Fig. 4).

On the basis of our findings we can presume that the complex possibly has the formula ((Bruc)$_2$•CoCl$_2$)•2H$_2$O.

In the case of brucine–NiCl$_2$ complex we have again in the IR spectrum a shift of the ν(C=O) vibration by 40 cm^{-1} lower than that of the free

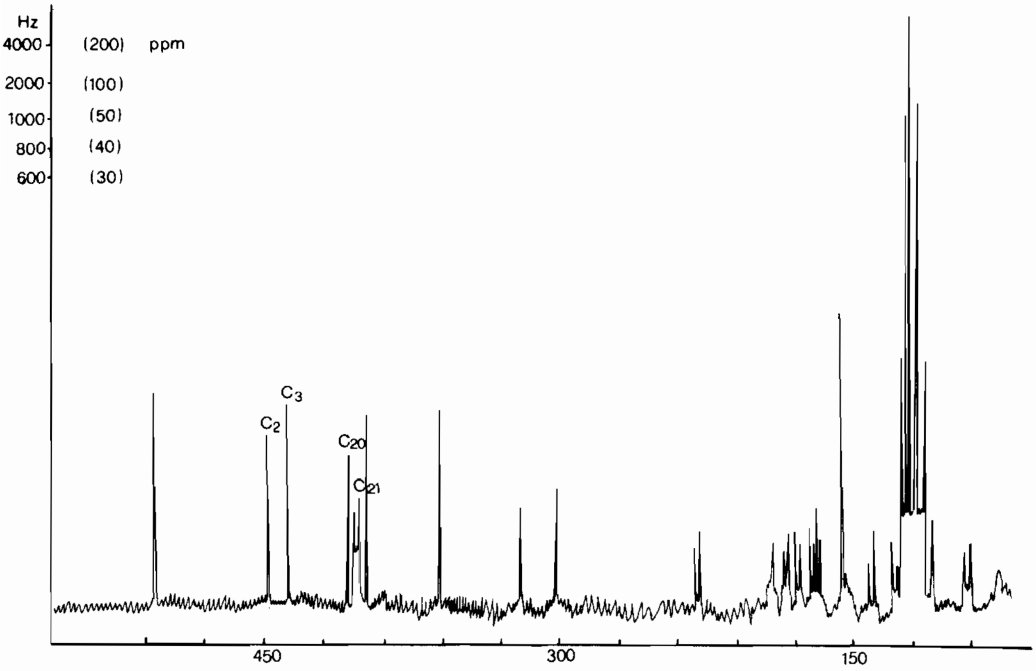

Fig. 2. ^{13}C-NMR spectrum of (bruc)PdCl/2 complex.

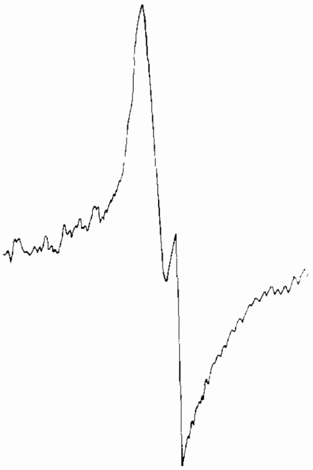

Fig. 3. $(Bruc)_2 \cdot CuCl_2$ complex.

ligand (for brucine the ν(C=O) appears at 1685 cm^{-1} while for the complex at 1647 cm^{-1}). A shift of the weak C–N vibrations of brucine at 1240 and 1220 cm^{-1} towards 1218 and 1200 cm^{-1} respectively is also observed in the spectrum of the complex. The complex is diamagnetic, and for this reason it does not give an ESR spectrum.

From these data we conclude that the most probable structure of the complex is square planar, with the nickel atom coordinated with the oxygen atom of the carbonyl and the nitrogen atom in the 9-position of the brucine molecule (Fig. 1). The possible formula of the compound is $(Bruc)_2 \cdot NiCl_2$.

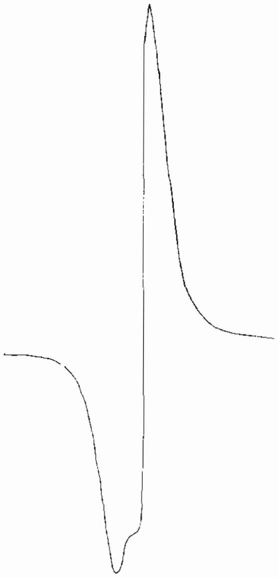

Fig. 4. $(Bruc)_2 \cdot CoCl_2 \cdot 2H_2O$ complex.

As a general conclusion (and a very remarkable one) we propose the inability of the tertiary nitrogen of brucine to coordinate with metal ions. The examined metals prefer to coordinate with oxygen or the π-electron cloud of the double bond (as in the case of Pd^{+2}). The nitrogen inability may be considered mainly as a steric one for two reasons:

(a) The approach of the metal ion and the formation of a stable coordination number are not possible because of the bulky molecule of brucine, and

(b) The distances between the two nitrogen atoms are not so favorable as to permit the formation of a stable bidentate ligand.[≠]

Acknowledgements

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[≠] According to a referee's comment the Ni-chelate is not stable due to the formation of a four membered ring. In order to examine if the proposed structure is true and to have a better and precise view of the molecule, we are now doing X-ray diffraction studies and our results will appear in a further communication.