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LETTER

Copper(II) and Cobalt(III) Complexes with Tetradentate Diimine Pyrrole Derivatives

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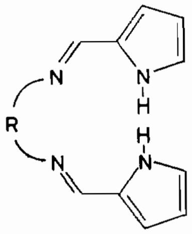
The chemistry of the metal complexes of the tetradentate diimine pyrrole derivatives has not been fully investigated. Only scant reports of syntheses by Pfeiffer *et al.* [1] and Von Stackelberg [2] of Ni(II) and Cu(II) complexes with two ligands of this type, and work by Weber [3] on Ni(II) complexes have been published. This paper presents the synthesis and characterization of a whole series (except two) of new copper and cobalt complexes with five tetradentate ligands (Scheme 1).



Scheme 1. R = *o*-phenylene, ophen(PimH)$_2$; ethylene, en(PimH)$_2$; propylene, pn(PimH)$_2$; butylene, bn(PimH)$_2$; pentamethylene, pa(PimH)$_2$.

Our initial purpose was the stabilization of higher oxidation states of transition metals through polydentate ligands, presenting by deprotonation a negative charge as well as a delocalized π-system. The influence of the bridging group (R) on the metal ion geometry has been studied in order to relate it to the oxidizability of the complexes.

Experimental

Preparation of the Ligands

The ligands were prepared according to the method described by Weber [3], which involved a condensation reaction of pyrrole 2-aldehyde and the appropriate diamine in a 2:1 molar ratio using ethanol as solvent. All the ligands were recrystallized in ethanol.

Preparation of the Compounds

Copper complexes

Complexes with en(PimH)$_2$, bn(PimH)$_2$ and pa(PimH)$_2$ were obtained using Pfeiffer's method [1]. The ligand and an aqueous ammoniacal copper sulfate solution in a ratio of 1:1 were refluxed in ethanol for 2 h. The solid complexes were isolated by filtration. The preparation of the complexes with ophen(PimH)$_2$ and pn(PimH)$_2$ is based on the method of Holm *et al.* [4]. Solid tetraethylammonium tetrachlorocuprate was added to an anhydrous tetrahydrofuran solution of the ligand (0.01 mole) and potassium t-butoxide (0.02 mole). The mixture was stirred 24 h at room temperature and filtered. The filtrate was evaporated to dryness. The crude solid copper complexes were purified by recrystallization from dichloromethane/n-hexane.

Cobalt complexes

All these compounds were prepared by Holm's method as described above using $[CoBr_4][NEt_4]_2$ as the metallic ion. After 24 h of stirring, diethyl ether was added to the oil obtained. After several hours, solids precipitated and were then recrystallized in a 30% CH_2Cl_2, 70% n-C_6H_{12} mixture.

Physical Measurements

Magnetic susceptibilities were determined at room temperature (20 °C) taking $HgCo(SCN)_4$ as reference; diamagnetic susceptibility corrections were calculated from Pascal's constants [5]. Infrared spectra were recorded on a Pye Unicam SP3 300 on KBr pellets.

Results and Discussion

Characterization data for all compounds prepared in this work are set out in Table 1.

Infrared spectra indicate clearly that the four nitrogen donor atoms are coordinated to the metal ion. The ligand N–H stretching vibration doublet centred near 3130 cm^{-1} disappears upon complex formation and the ligand C=N stretching frequency at 1640 ± 5 cm^{-1} with aliphatic R bridging and at 1600 cm^{-1} with aromatic R bridging is shifted downfield by 50 ± 5 cm^{-1} after complexation.

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TABLE 1. Analytical and physical data

Compounds	Colour	Melting point (°C)	$10^6\chi_M$(Corr) (c.g.s.u.)	C (%)		H (%)		N (%)		ν(C=N) (cm^{-1})
				Calc.	Found	Calc.	Found	Calc.	Found	
ophen$(PimH)_2$	yellow	194		73.26	73.26	5.38	5.27	21.36	21.47	1600
en$(PimH)_2$	white	183		67.26	67.10	6.59	6.51	26.15	26.15	1640
pn$(PimH)_2$	white	124		68.42	68.78	7.06	7.26	24.54	24.45	1635
bn$(PimH)_2$	white	181		69.39	69.38	7.49	7.63	23.12	23.07	1645
pa$(PimH)_2$	white	144		70.28	70.00	7.86	7.95	21.86	21.79	1645
Cuophen$(Pim)_2$	red	265	1570	59.34	59.41	3.73	3.67	17.30	17.32	1550
Cuen$(Pim)_2$	dark green	203	1560	52.26	52.60	4.38	4.29	20.32	19.95	1590
Cupn$(Pim)_2$	dark brown	185	1850	53.88	53.94	4.84	5.03	19.34	19.41	1590
Cubn$(Pim)_2$	dark brown	154	1530	55.34	55.54	5.31	5.44	18.44	18.48	1600
Cupa$(Pim)_2$	dark green	137	1560	56.69	56.96	5.67	5.31	17.63	17.60	1600
$[Et_4N]$[Coophen$(Pim)_2Br_2$]	dark orange	198 dec	dia[b]	47.31	47.70	5.26	5.75	11.50	11.34	1550
K[Coophen$(Pim)_2Br_2$] [a]	dark orange	202 dec	dia	37.08	37.24	2.32	2.23	10.81	10.94	1590
$[Et_4N]$[Coen$(Pim)_2Br_2$]	dark orange	155 dec	dia	42.80	42.40	5.71	5.45	12.48	12.07	1585
K[Coen$(Pim)_2Br_2$] [a]	dark orange	168 dec	dia	30.65	30.83	2.57	2.84	11.92	11.54	1585
K[Coen$(Pim)_2Cl_2$] [a]	dark orange	162 dec	dia	37.80	38.09	3.15	3.45	14.70	15.07	1590
Co_2[bn$(Pim)_2]_3$	pale orange	182	dia	60.15	60.29	5.73	5.94	20.05	19.78	1590
Co_2[pa$(Pim)_2]_3$	pale orange	179	dia	61.35	61.28	6.18	6.75	19.08	18.84	1590

[a] Cobalt compounds with K^+ as cation were obtained using anhydrous Co(II) halides. [b] Dia = diamagnetic.

Magnetic data are consistent with Cu(II) compounds ($\mu_B \approx 1.9$ BM) and Co(III) d^6 diamagnetic complexes. All the Cu(II) compounds are probably square-planar, as Von Stackelberg [2] has shown for the only two Cu(II) compounds described in the literature, Cuen$(Pim)_2$ and Cuophen$(Pim)_2$. The diamagnetism of the cobalt compounds indicates that the cobalt(II) metallic ion is spontaneously oxidized in Co(III). The nature of the new cobalt compounds depends only on the length of the bridging chain. When the bridging chain is short (two carbon atoms, ethylene or *o*-phenylene) monomeric species are obtained: the presence of the Et_4N^+ cation has been shown by NMR, which involves the coordination of two bromide atoms. In the case of the larger bridging chain, bn$(PimH)_2$ and pa$(PimH)_2$, we have shown the absence of both the Et_4N^+ cation and halides and we must consider the existence of the dimeric species Co_2L_3. Infrared spectra are practically the same for all cobalt compounds, excluding bridging nitrogen atoms, and suggest that the ligand is coordinated through a pyrrole 2-aldimine group on each Co(III) ion with the alkyl chain as a bridge. This hypothesis is also supported by the fact that no compound can be prepared with the intermediate pn$(PimH)_2$ ligand.

Although the oxidation of Co(II) in Co(III) is spontaneous during the complex synthesis, all attempts with Fe^{3+} ion or I_2 to further oxidize Cu(II) and Co(III) compounds failed, the ligands being destroyed during the chemical oxidation.

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