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Complexes of Divalent Metal Halides with Benzo[c]-cinnoline-N,N′-dioxide

N. F. ALBANESE and H. M. HAENDLER*

Department of Chemistry, University of New Hampshire, Durham, N.H. 03824, U.S.A.

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Complexes of benzo[c]cinnoline-N,N′-dioxide (L) with some divalent metal halides have been prepared. Although coordination complexes of heteronuclear aromatic amine N-oxides [1–8] and of azo compounds [9–11] are well-known, the coordination chemistry of azodioxy ligands has not been described. Benzo[c]cinnoline-N,N′-dioxide is of particular interest as a ligand because it is structurally analogous to 9,10-phenanthrenequinone, which forms intensely colored complexes with divalent metal halides [12], and greenish-black zero valent iron, cobalt, and nickel complexes [13].

Benzo[c]cinnoline-N,N′-dioxide and the corresponding monoxide are intermediates in the reduction of 2,2′-dinitrobiphenyl to benzo[c]cinnoline [14–18]. The procedure of Ross and Kuntz [14] was followed in the preparation of L. The ligand was separated from the reaction mixture by column chromatography and further purified by recrystallization. The melting point of crystals grown from t-butanol/methanol solution was 246–248 °C with decomposition, compared to 233–236 °C reported by Ross *et al.* [19], and to 249–250 °C reported by Kemper and Castle [15]. Elemental analysis (Table I) and X-ray powder diffraction [20] further identified the product as benzo[c]cinnoline-N,N′-dioxide.

Zinc(II) bromide and copper(II) bromide solutions were prepared by direct bromination in methanol [12]. Commercially available anhydrous cadmium chloride and mercuric chloride were used. The cadmium chloride was dissolved in methanol which contained about 10% acetic anhydride as a drying agent, whereas the mercuric chloride was dissolved in glacial acetic acid. The metal halide complexes were prepared by adding a hot, filtered solution of L in glacial acetic acid to a concentrated solution of the metal in a 1:1 ligand–metal mol ratio. The complex $ZnLBr_2$ immediately precipitated and was filtered from the hot solution. A second complex, ZnL_2Br_2, formed as the filtrate cooled. The cadmium and copper complexes, $CdLCl_2$ and $CuLBr_2$, precipitated immediately from hot solution as fine powders, whereas the mercury complex, $HgLCl_2$, crystallized as long needles as the solution cooled. The precipitates were washed with pentane, hexane, or petroleum ether and dried *in vacuo.* Elemental analysis (Table I), X-ray powder diffraction, and infrared spectroscopy demonstrated that the precipitates are unique complexes. Thermogravimetric analysis showed the absence of adsorbed or coordinated solvent molecules in each complex.

Preparation of copper-doped zinc complexes was initially attempted as for zinc bromide, with about 1.5 mol% copper metal dust added to the zinc in the bromination step. Only copper-doped $ZnLBr_2$ was prepared in this manner, indicating selective complexation of copper in the first phase of the reaction. In a second attempt to prepare copper-doped ZnL_2Br_2, copper(II) acetate in glacial acetic

TABLE 1. Analytical Data.

Compound	Color	Analysis					
		%C		%H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
Ligand	white	67.91	68.00	3.81	3.65	13.20	13.06
$CuLBr_2$	brick red	33.09	35.92	1.85	2.22	7.08	7.08
$ZnLBr_2$[a]	orange	32.94	32.82	1.84	1.83	6.40	6.36
$ZnLBr_2$	orange	32.94	32.85	1.84	1.80	6.40	5.92
ZnL_2Br_2	rust	44.36	44.10	2.48	2.64	8.62	8.43
$CdLCl_2$	peach	36.43	37.15	2.04	2.06	8.10	6.95
$HgLCl_2$	orange	29.79	30.31	1.67	1.76	5.79	5.62

[a] Doped with approximately 1% Cu^{2+}.

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*Author to whom correspondence should be addressed.

TABLE II. Decomposition Temperatures.

Complex	Decomposition Temperature (°C)	Corresponding Halide	M.P. °C
$CuLBr_2$	345	$CuBr_2$	498
$ZnLBr_2$	432	$ZnBr_2$	394
ZnL_2Br_2	392	$ZnBr_2$	394
$CdLCl_2$	384	$CdCl_2$	868
$HgLCl_2$	256	$HgCl_2$	276

acid was added to a hot, filtered solution of ZnL_2Br_2 in glacial acetic acid. The crystalline product had the same stoichiometry as ZnL_2Br_2, but no copper could be detected by EPR spectroscopy.

Although some complexes with N-oxide ligands are light-sensitive [7, 21], the coordination complexes of benzo[c]cinnoline-N,N-dioxide are stable in air and strong sunlight with no evidence of decomposition after 1–2 years. However, these complexes decompose in water, with formation of the white insoluble ligand. The order of lability of these complexes with respect to decomposition in water is

$$CuLBr_2 \cong ZnLBr_2^2 > ZnL_2Br_2 > CdLCl_2 \gg HgLCl_2.$$

The $CuLBr_2$ and $ZnLBr_2$ complexes react immediately, whereas $HgLCl_2$ shows no evidence of decomposition in water or strong acid after several hours. The cadmium and copper complexes are insoluble in nitromethane whereas the zinc and mercury complexes are limitably soluble ($<10^{-2}$ *M*). The copper complex is unstable in more polar solvents such as N,N-dimethylformamide, as indicated by the identity of the visible absorption and EPR spectra of the copper complex with those of copper(II) bromide in the same solvent.

Unlike the intensely colored violet, brown, or black metal halide complexes of phenanthrenequinone [12] wth zinc, cadmium, and mercury, respectively, the complexes of benzo[c]cinnoline-N,N′-dioxide are uniformly red or orange. Generally, in complexes of aromatic amine N-oxides the M–O–N angle is about 114–120° [22]. Thus, the difference in color between complexes with L and complexes with phenanthrenequinone probably arises from less efficient metal–ligand charge transfer in the former due to tilting of the metal–oxygen bond out of the plane of the ligand.

Conductivity measurements at 25 °C of nitromethane solutions ($0.7–3 \times 10^{-3}$ *M*) showed that the zinc and mercury complexes do not dissociate as weak electrolytes. Equivalent conductivities were small (~1–7 ohm^{-1} cm^2 $equiv^{-1}$) and independent of concentration. In contrast, metal perchlorate [3–6, 8, 22], nitrate, iodide, and bromide [7] complexes with N-oxide ligands usually behave as strong electrolytes, whereas copper(II) and cobalt(II) chloride complexes with bipyridine-N,N′-dioxide [7] and various divalent metal chloride complexes with bipyridine-N-oxide [2] behave as weak electrolytes.

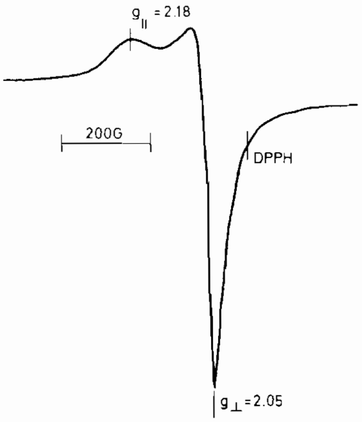


Fig. 1. EPR spectrum of polycrystalline $CuLBr_2$ (room temperature).

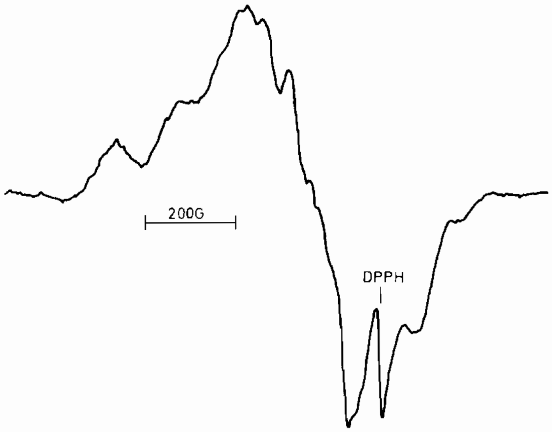


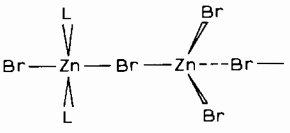
Fig. 2. EPR spectrum of copper-doped polycrystalline $ZnLBr_2$ (room temperature).

The decomposition temperatures of the complexes measured by integration of the temperature–weight loss curves [23] are compared to the melting points of the corresponding metal halides in Table II. The much higher decomposition temperature of $ZnLBr_2$ relative to the other complexes, and relative to the melting point of zinc(II) bromide, is indicative of an ionic, rather than molecular, structure, and supports formulation of this complex on an ion pair such as $[ZnL_2]^{2+}[ZnBr_4]^{2-}$. This structure is analogous to the proposed structure of the zinc(II) bromide complex with phenanthrenequinone [12]. Comparison of the X-ray diffraction data of the 1:1 zinc bromide complexes with the two ligands suggests that these two complexes have similar structures. The low conductivity of the $ZnLBr_2$ complex in nitromethane probably arises from strong ion-pairing in solution.

The copper complex in polycrystalline form has a room temperature magnetic moment of 1.85 B.M., which is characteristic of copper complexes in the absence of exchange coupling [24]. In contrast, the room temperature magnetic moment of anhydrous copper(II) bromide is 1.31 B.M. [25], and numerous copper(II) complexes with N-oxide ligands are known which have subnormal magnetic moments arising from exchange coupling.

The polycrystalline EPR spectrum of $CuLBr_2$ (Fig. 1) has the characteristic lineshape corresponding to axial symmetry [24], and the following parameters: $g_\perp = 2.05$ and $g_\parallel = 2.18$. A $d_{x^2-y^2}$ or d_{xy} ground state is indicated: thus, the coordination geometry around the copper(II) ion is either elongated octahedral, square planar, or less commonly, compressed tetrahedral.

The EPR spectrum of the copper(II) ion in the diamagnetic host lattice of the $ZnLBr_2$ complex is shown in Fig. 2. Computer simulation of the spectrum suggests the presence of two unequivalent magnetic sites: site 1 has $g_\perp = 2.08$, $g_\parallel = 2.27$, $a_\perp = 35$ G and $a_\parallel = 150$ G, while site 2 has $g_\perp = 2.0$, $g_\parallel = 2.27$, $a_\perp = 80$ G, and $a_\parallel = 130$ G. These parameters can be approximated only roughly due to the broadness of the spectrum, which can be attributed to strong bromine nuclear hyperfine interactions. Splittings of about 20–30 G arising from these interactions can be discerned. Unlike site 1 which has parameters corresponding to a $d_{x^2-y^2}$ or d_{xy} ground state, site 2 has parameters corresponding to a d_{z^2} ground state, and thus, compressed tetragonal–octahedral geometry. Thus, the EPR results concur with crystallographic, conductivity, and thermal data, and suggest the structure shown below for $ZnLBr_2$.



compressed octahedral   tetrahedral

This structure is apparently not shared by $CuLBr_2$ because it would probably give rise to exchange interactions between neighboring copper(II) ions which are not observed.

Little information is available regarding the structures of $HgLCl_2$ and $CdLCl_2$. The insolubility of the cadmium complex suggests that this complex is polymeric. Bridging by benzo[c]-cinnoline-N,N′-dioxide, producing an *anti–anti* configuration with respect to coordination through oxygen, with cadmium and mercury, is not unexpected because of the larger ionic radii of these metal cations. Therefore, $HgLCl_2$ is probably dimeric.

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