BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 791—793 (1967)

Studies on Pentakisantipyrine Copper(II) Perchlorate

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(Received April 11, 1966)

Five coordinated antipyrine (A) complex of copper(II) perchlorate, $[CuA_5](ClO_4)_2$ has been prepared. Both the electric conductivity and the cryoscopic determination of molecular weight in nitrobenzene solution show that the complex dissociates into three ions. Differential thermal analysis gives one peak at about 285°C owing to the explosion of the complex. Infrared spectrum reveals the presence of both strongly and weakly coordinated antipyrine molecules in the complex. The complex in 1, 2-dichloroethane absorbs at 16130 ($\varepsilon=51$), 15630 ($\varepsilon=53$) and 14500 ($\varepsilon=56$) cm^{-1}. These d-d transitions with comparatively high intensities suggest C_{4v} symmetry for the complex ion $[CuA_5]^{2+}$. A square pyramidal structure with four antipyrine molecules in the square plane at normal Cu-O bond distance and one antipyrine occupying the axial position with an elongated Cu-O bond, is assigned to the complex ion.

Metal antipyrine complexes were first prepared by Dorfurt and Schliephake.[1] But a systematic investigation of these complexes has not been carried out so far. In this laboratory,[2] it was found that the antipyrine complex of copper(II) perchlorate was different from the other transition metal perchlorate complexes prepared. The former took five antipyrine molecules per copper ion, whereas the latter took six per metal ion. An investigation of the copper complex was undertaken to assign a structure to it. The complex was prepared, analysed and its magnetic, spectral and thermal properties were studied. Its electric conductivity and molecular weight by cryoscopic method in nitrobenzene solution were determined.

Experimental

Materials Employed. (1) $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared from copper(II) oxide and perchloric acid.[3]

(2) Antipyrine (1-phenyl, 2, 3-dimethyl 5-pyrazolone, henceforth abbreviated as A) was Merck reagent of 99.8% purity.

Preparation of the Complex. To an aqueous solution of copper perchlorate hexahydrate (~0.1 M), an excess of aqueous antipyrine solution (10%) was added dropwise. The solution turned green, while stirring. The solution was allowed to stand overnight, when green crystals of the complex separated out. The supernatent liquid was decanted off, the crystals were recrystallised from water, dried *in vacuo* over fused $CaCl_2$ and analysed.

Copper in the complex was estimated gravimetrically[4] as $Cu(Py)_2(SCN)_2$. This method was found to be convenient since antipyrine does not interfere. Antipyrine in the complex was determined by Bougault's method modified by Kolthoff,[5] correction being made for the iodine consumed by copper forming Cu_2I_2. Perchlorate was estimated by Kurz's method.[6]

Found: Cu, 5.3; A, 78.2; ClO_4^-, 16.6%. Calcd for $CuA_5(ClO_4)_2$: Cu, 5.27; A, 78.18; ClO_4^-, 16.59%.

The compound is a green crystalline non-hygroscopic solid, soluble in acetonitrile, chloroform, *etc.*, sparingly soluble in water and insoluble in non-polar solvents like benzene.

Apparatus and Procedure. Magnetic susceptibility: The magnetic moment of the complex was determined at room temperature by Gouy method[7] using mercury(II) tetrathiocyanato cobaltate(II) as the calibrant.

Differential Thermal Analysis (DTA): The DTA study was carried out with a standard manual apparatus,[8] using a chromel-alumel thermocouple. As the complex was found to be explosive, it was mixed with alumina in a ratio 1 : 10 to minimise the impact of explosion. The heating rate was maintained at 10± 1°C per minute.

Conductance and Molecular Weight Determination: The electric conductivity of the complex in pure dry nitrobenzene was measured at 25°C using Siemen's conductivity bridge and a conventional diptype conductance cell with a cell constant 0.600 cm^{-1}, employing platinum-black electrodes. The molecular weight of the complex was determined in the same solvent by Beckmann's freezing point method.

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Infrared and Electronic Spectra: The infrared spectrum in KBr disc was recorded with Carl Zeiss UR 10 spectrophotometer, equipped with KBr, NaCl and LiF prisms. The visible electronic spectra of the complex in pure dry 1, 2-dichloroethane, acetone and acetonitrile were taken with Hilger-Uvispek spectrophotometer, model H 700, using a pair of 1 cm matched quartz cells. The ultraviolet spectrum was observed in acetonitrile.

Results and Discussion

The molar conductance of the complex in nitrobenzene in the concentration range 10^{-3} to 10^{-4} M at 25°C is around 40 $ohm^{-1}\,cm^2\,mol^{-1}$. The value corresponds to 1 : 2 dissociation of the complex,[9] expressed as:

$$[Cu\ A_5]\ (ClO_4)_2 \rightarrow [Cu\ A_5]^{2+} + 2ClO_4^-$$

The molecular weight of the complex in the concentration range 10^{-2} to 10^{-3} M in the same solvent is around 390. A value of 400 is expected according to the 1 : 2 type dissociation, as given above.

The differential thermal analysis of the complex gives an exothermic peak around 285°C due to its explosion, when antipyrine molecules are oxidised by the oxygen liberated from the perchlorate. The explosion temperature is above the exothermic decomposition temperature of $Cu(ClO_4)_2 \cdot 6H_2O$[10] which occurs at 252°C. The complex does not show any endothermic peak near the melting point of antipyrine at 114°C, showing the absence of any uncoordinated antipyrine molecule in the complex. The cryoscopic determination of the molecular weight of the complex does not show any free antipyrine in nitrobenzene solution either.

The assignment of infrared absorption frequencies for the complex is given in Table 1. Most of the bands are assigned considering the monosubstituted benzene ring[11] and the five-membered pyrazolone ring system.[12]

The antipyrine complex gives two bands, a strong one at 1610 cm^{-1} and shoulder at 1655 cm^{-1}, both being attributable to the C=O stretch of coordinated antipyrine. The lowering of C=O stretch from 1666 of free antipyrine[13] to 1610 and 1655 cm^{-1} in the complex indicates that coordination of antipyrine to copper is through the carbonyl oxygen. These two bands are not observed in the antipyrine complex of $CuCl_2$, $[CuCl_2 \cdot 2A]$ and in other six-coordinated antipyrine complexes of alkaline earths and transition-metal perchlorates studied in this laboratory.[2] It seems that the strong band at 1610 cm^{-1} is due to the strongly coordinated antipyrine, while the shoulder at 1655 cm^{-1} is due to the weakly bonded antipyrine.

TABLE 1. ASSIGNMENT OF INFRARED FREQUENCIES OF THE COMPLEX

Frequency, cm^{-1}	Assignment
1655 m, sh	ν(C=O) of weakly coordinated antipyrine
1610 VS	ν(C=O) of strongly coordinated antipyrine
1585 S	Pyrazolone ring stretching.
1500 S	ν(C=N)
1430 w, 1420 m	Bending of pyrazolone skeleton
1375, 1350, 1325 w	$\delta_a(CH_3)$
1300, 1270, 1180, 1148 w	δ(C-H)
1040 w	CH_3 rock
1015, 995 w	Ring breathing of benzene
1100 VS	ν_3 ClO_4
935 w	ν_1 ClO_4
870 m	New band arising on complex formation
810 w, sh; 890 m, sh	ν_s(C-C)
778 S, 730 m, 700 S	C-H out-of-plane deformation of monosubstituted benzene
660 m	CH rock
625 m	ν_4 ClO_4

VS=Very strong, S=strong, m=medium
w=weak, ν=stretch, ν_a=asymmetric stretch, ν_s=symmetric stretch, sh=shoulder, δ=in-plane deformation

The appearance of unsplit ν_3 and ν_4 bands of perchlorate in the solid state at 1100 and 625 cm^{-1} respectively shows T_d symmetry of the perchlorate group and its ionic character in the complex. The appearance of the forbidden ν_1 weak band of perchlorate at 935 cm^{-1} may be due to the crystal field effect. Such a weak band is observed even in potassium perchlorate.[14]

The complex dissolved in 1, 2-dichloroethane (1.05×10^{-3} M) shows two shoulders at 16130 cm^{-1} (ε=51) and 15630 cm^{-1} (ε=53) and a band at 14500 cm^{-1} (ε=56). The appearance of three

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weak bands can be explained by a square pyramidal structure having C_{4v} symmetry of the complex ion. The relative order of d-orbitals in such a system is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$. Accordingly the bands at 16130, 15630 and 14500 cm^{-1} are due to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions respectively. This assignment is supported by the solvent effect on the observed bands as given in Table 2.

TABLE 2. SOLVENT EFFECT ON d-d TRANSITIONS OF $[CuA_5]^{2+}$ ION

Solvent	$\nu_1 cm^1(\varepsilon)$	$\nu_2 cm^{-1}(\varepsilon)$	$\nu_3 cm^{-1}(\varepsilon)$
1, 2-Dichloroethane	16130(51)	15630(53)	14500(56)
Acetone	15020(45)	15880(48)	13160(50)
Acetonitrile	—	—	12820(48)

The coordination of a solvent molecule in the sixth position along the z-axis would increase the ground state energy of the complex ion. From the spatial disposition of the d-orbitals, it is evident that the d_{z^2} orbital would be more affected than the degenerate d_{xz} and d_{yz} orbitals, on coordination of the solvent molecule. Hence the bands due to transitions $d_{z^2} \rightarrow d_{x^2-y^2}$ (ν_3) and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (ν_1) undergo a red shift, as the coordinating power of the solvent increases. Further, the shift for $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is larger than that for $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, as expected (Table 2). The transition $d_{xy} \rightarrow d_{x^2-y^2}$ (ν_2) should not be much affected, as a large change due to the solvent effect is not expected in the xy-plane. Thus the solvent shifts can best be rationalized in terms of the C_{4v} symmetry of the complex ion.

The molar extinction coefficient of about 60 for the main band in the non-polar solvent (1, 2-dichloroethane) is more than expected for a centrosymmetric copper(II) complex. Usually, in non-polar solvents like chloroform, copper(II) complexes[16-18] with four oxygen donors in a square plane have molar extinction coefficients of about 30. The same compounds in coordinating solvents like pyridine show increased intensities[19] (~60) and this is attributed to the coordination of the solvent molecule in the z-axis which removes the centre of symmetry of the square planar molecule. Graddon[17] has shown that an increase in intensity of the square planar complex is due to the formation of square-pyramidal base adducts in coordinating solvents like pyridine. The high molar extinction coefficient values of the d-d transition for the present complex may be attributed to the presence of an acentric $[CuA_5]^{2+}$ ion in the complex.

In the ultraviolet region, the complex in acetonitrile has two strong absorption bands at 43480 cm^{-1} (log $\varepsilon = 4.75$) and 35720 cm^{-1} (log $\varepsilon = 4.62$). Pure antipyrine in the same solvent shows bands at 41680 and 35970 cm^{-1}. The band undergoing hypsochromic shift is expected to be mainly associated with the C=O group of antipyrine, since it is responsible for coordination with the metal ion.

The molar magnetic susceptibility χ_M of the complex was found to be 1228×10^{-6} cgs units and the correction for diamagnetism 647×10^{-6} cgs units. The coorected molar susceptibility for the complex at 27°C was therefore, 1875×10^{-6} cgs units. Hence the magnetic moment is 2.12 B. M. The value is in the expected range (2.1—2.2 B. M.) for a five-coordinated square pyramidal copper (II) complex.[20] The electron spin resonance studies of this complex by Srinivasan *et al.*[21] have shown $S = 1/2$, the unpaired electron being in the $d_{x^2-y^2}$ orbital. The copper ion is shown to be in the tetragonal environment with $g_{\parallel} = 2.40$ and $g_{\perp} = 2.07$. These observations also support the square pyramidal configuration for the complex.

In general, five-coordinate complexes can be either square-pyramidal or trigonal bipyramidal. X-Ray diffraction studies of single crystals have indicated that most of the five-coordinate complexes of copper(II) are square-pyramidal,[22-24] although a trigonal bipyramidal structure is also reported.[25] According to Gillespie,[26] due to the interelectronic repulsion, a square pyramidal arrangement is more stable than a bipyramidal one, if the d-shell is a prolate ellipsoid. The presence of the unpaired electron in the $d_{x^2-y^2}$ orbital as found by the ESR studies of the complex,[21] indicates a prolate ellipsoidal arrangement for the d-shell. The most favourable structure for the complex ion is, therefore, a square pyramidal one with four normal Cu-O bonds in the square plane and an elongated axial Cu-O bond, as found by the two infrared carbonyl stretching frequencies at 1610 and 1655 cm^{-1} respectively. Such a structure finds support from the electronic absorption spectrum also.

The authors thank Professor M. R. A. Rao for his interest in the work.

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