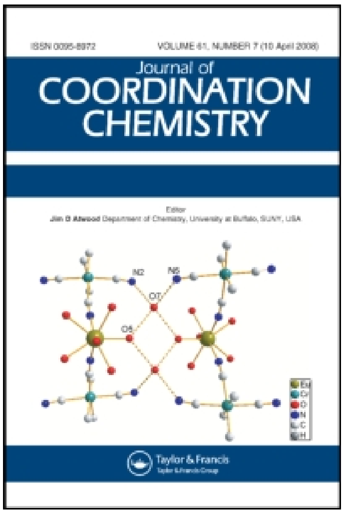

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Syamal, A. and Theriot, L. J.(1973) 'Copper(II) Complexes of N-(Hydroxyethyl)Salicylideneimines', Journal of Coordination Chemistry, 2: 3, 241 — 242
To link to this Article: DOI: 10.1080/00958977308072980
URL: http://dx.doi.org/10.1080/00958977308072980

J. Coord. Chem., 1973, Vol. 2, pp. 241–242

Printed in Woking, England

Copper(II) Complexes of N-(Hydroxyethyl)Salicylideneimines

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(*Received May* 22, 1972; *in final form August* 9, 1972)

INTRODUCTION

Two groups of workers[1,2] have described the synthesis of Cu(sal:propanolamine). The compound is a dimer in chloroform and has a magnetic moment of 0.49 BM at room temperature.[2] There is no report in the literature on the synthesis of Cu(sal:ethanolamine). Apparently several groups have tried to synthesize the compound without success.[2,3] This communication describes the successful synthesis and characterization of Cu(sal:ethanolamine) and Cu(5-Br-sal:ethanolamine).

RESULTS AND DISCUSSION

When copper(II) acetate monohydrate and the Schiff base 5-X-salicylaldehyde:ethanolamine were refluxed in methanol, compounds of the type Cu(5-X-sal-ethanolamine)·H_2O were obtained[4] (X = H or Br). Infrared spectra show the presence of coordinated water in these compounds (ν (OH) band at ~ 3400 cm^{-1}). Cu(sal:ethanolamine)·H_2O was dissolved in a minimum amount of pyridine-water mixture (90:10). Partial evaporation on a water bath resulted in the separation of green microcrystals of Cu(sal:ethanolamine)·Py (where Py = pyridine). For the preparation of Cu(5-Br-sal:ethanolamine) the aquo compound was dissolved in a minimum amount of pyridine. Addition of water to the pyridine solution resulted in the precipitation of the pyridine adduct. The pyridine adducts were dried at 150°C under vacuum for 24 hours. Complete elimination of pyridine takes place at this temperature. Anal.[5] calcd. for Cu(sal:ethanolamine), $CuC_9H_9NO_2$, C, 47.68; H, 3.97; N, 6.18. Found: C, 47.39; H, 3.97; N, 5.96. Calcd. for Cu(5-Br-sal:ethanolamine), $CuC_9H_8NO_2Br$, C, 35.35; H, 2.62; N, 4.58. Found: C, 35.52; H, 2.71; N, 4.46%. The characteristic ν (OH) band is absent in the infrared spectra of these complexes.

Molecular weight measurements in spectral grade chloroform solutions indicate that both complexes are tetrameric (Calcd. for $[Cu(sal:ethanolamine]_4$, 906. Found: 958 Calcd. for $[Cu(5\text{-}Br\text{-}sal:ethanolamine]_4$, 1222. Found: 1267. The electronic spectra of the complexes exhibit a broad absorption band around 16,000-16,500 cm^{-1} in both nujol mull and chloroform solutions ($\varepsilon = 130$–148 1. $mole^{-1}$. cm^{-1}). This band is assigned to the d-d transitions.

The magnetic susceptibilities and magnetic moments of the complexes from 78 to 292°K are presented in Table I. The magnetic moments of the

TABLE I

Magnetic susceptibilities and magnetic moments of copper(II) complexes[a, b, c]

Cu(sal:ethanolamine)			(Cu(5-Br-sal:ethanolamine)		
Temp. (°K)	X_M^{corr} (10^{-0}cgs unit)	μ_{eff} (BM)	Temp. (°K)	X_M^{corr} (10^{-6}cgs unit)	μ_{eff} (BM)
294	1422	1.83	292	1480	1.86
265	1585	1.84	265	1647	1.87
228	1857	1.85	228	1916	1.87
189	2270	1.86	189	2429	1.92
152	2863	1.87	152	3129	1.93
120	3600	1.87	120	4165	2.01
78	5709	1.89	78	6618	2.04

[a] Magnetic susceptibilities were determined by the Gouy method.

[b] Magnetic moment was calculated using the Curie equation: $\mu_{eff} = 2.84(X_M^{corr} \times T)^{1/2}$ BM. The precision of the measured magnetic moments is $\pm$ 2% or better.

[c] TIP = 50 × 10^{-6} cgs units.

complexes increased slightly as the temperature was lowered. Approximating the magnetic properties using the Bleaney and Bowers equation[6] gave positive J values ($J = +16\ \text{cm}^{-1}$ for Cu(sal:ethanolamine), $J = +64\ \text{cm}^{-1}$ for Cu(5-Br-sal:ethanolamine); $g_{av} = 2.1$ and TIP $= 50 \times 10^{-6}$ cgs units were used). The positive J values and the increase in magnetic moment with the lowering of the temperature are indicative of ferromagnetic coupling in these complexes.[7,8] The electron spin resonance spectrum of Cu(sal:ethanolamine) in polycrystalline solid at 77°K exhibits four lines at about 625, 1840, 5350, and 7200 G. The other complex, Cu(5-Br-sal:ethanolamine) exhibits 5 lines in powdered sample (77°K) at about 640, 1760, 3266, 5570, and 7150 G. The extra line at 3260 G is attributed to the spin-doublet monomeric copper(II) impurity present in this complex.[8,9] The other four lines are assigned to the H_{z_1}, $\Delta M_s = 2$, $H_{\perp_2}$, and H_{z_2} lines respectively. We assumed that E of these complexes is so small as to be considered zero.

The magnetic properties of Cu(sal:ethanolamine), Cu(sal:propanolamine) are analogous to the corresponding acetylacetone derivatives. Cu(acac:ethanolamine) and Cu(acac:propanolamine) have magnetic moments 1.87 and 0.41 BM respectively at room temperature.[10] Bertrand and Kelley[10] have recently described the structure of Cu(acac:ethanolamine) and Cu(acac:propanolamine). In Cu(acac:ethanolamine) the oxygen is tetrahedrally coordinated and in Cu(acac:propanolamine) the oxygen is planar. The former has two tetramers per unit cell and the latter has two dimers per unit cell. As the magnetic properties of these two series of complexes are similar we propose a structure similar to Cu(acac:ethanolamine) for Cu(sal:ethanolamine) and Cu(5-Br-sal:ethanolamine). Molecular weight data also supports a tetrameric structure. It is interesting to note that Cu(sal:propanolamine) is a dimer and is involved in antiferromagnetic exchange. On the other hand, Cu(cal:ethanolamine) is a tetramer and is involved in ferromagnetic interaction. This difference in magnetic properties may be related to the presence of different structures in these two complexes; two different types of copper(II) ions and two different types of bridging oxygens.[10]

ACKNOWLEDGEMENTS

This research was supported by the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund.

REFERENCES AND NOTES

1. S. Yamada, Y. Kuge and K. Yamanouchi, *Inorg. Chim. Acta* **1,** 139 (1967).
2. M. Kato, Y. Muto, H. B. Jonassen, K. Imai and A. Harano, *Bull. Chem. Soc., Japan* **41,** 1864 (1968).
3. A. Nakahara, H. Yamamoto and H. Matsumoto, *Sci. Rep., College of Gene. Educ., Osaka Univ.* **12,** 11 (1963); *Chem. Abstr.* **62,** 215e (1965).
4. Cu(sal:ethanolamine)·H_2O is a spin-doublet species and obeys the Curie-Weiss law with $\theta = 30°$K. μ_{eff} at 298°K = 1.81 BM.
5. Analyses were done by Galbraith Laboratories Inc., Knoxville, Tennessee.
6. B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* **A214,** 451 (1952).
7. A. T. Casey, B. F. Hoskins and F. D. Williams, *Chem. Comm.* 904 (1970).
8. J. A. Barnes, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.* **11,** 144 (1972).
9. J. R. Watson, C. Shyr and C. Trapp, *Inorg. Chem.* **7,** 469 (1968).
10. J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta* **4,** 203 (1970).