Magnetic and Spectroscopic Behaviour of Copper(II) Complexes of 5-Substituted 2-Salicylidenebiguanides

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Copper(II) complexes of 2-salicylidenebiguanide (salbg) and its 5-substituted derivatives R-salbg (R = Me, Et, Ph, or 2Et) have been studied by magnetic and spectroscopic methods. The magnetic moments and magnetic-susceptibility values over the range 80—310 K indicate antiferromagnetic interaction in these complexes. Attempts have been made to fit the data to models suggested for polynuclear Cu^{II} complexes. The analysis reveals that the degree and nature of polymerisation vary with substitution on the biguanide moiety. With increase in size of the substituent, the complexes change from a trimeric to a dimeric form. Higher ligand-field band positions in the electronic spectra of the complexes indicate a distorted square-planar structure. The i.r. spectra suggest phenoxide bridging.

ALKYL and aryl carboxylates of copper(II) are the most extensively studied complexes having aniferromagnetic interaction. The behaviour of these complexes in a magnetic field has been thoroughly discussed by Kato *et al.*[1] An equation has been proposed by Jotham *et al.*[2] for copper carboxylates which takes into consideration the various possible interactions.

Recently Schiff-base complexes of Cu^{II} have received considerable attention. Calvin [3] reported subnormal magnetic-moment values for salicylideneiminatocopper(II) as early as 1946. Exchange interactions in many Schiff-base Cu^{II} complexes have been found by Kishita and his co-workers [4-6] from the measurement of their magnetic susceptiblities. Magnetic and spectroscopic properties of a mixture of copper(II) chloride and *N*-ethylsalicylideneiminatocopper(II) have been investigated by Tokii *et al.*[7] Figgis and Martin [8] indicated the degree of polymerisation from the magnetic studies on bis[*NN'*-ethylenebis(salicylideneiminato)]copper(II) complexes. The binuclear structure of N-substituted salicylideneiminato-complexes of Cu^{II} with $CuCl_2$ was predicted from their behaviour in a magnetic field.

Lower magnetic moments at room temperature have been observed for salicylidenebiguanidecopper(II) complexes.[9] It was of interest to study the magnetic properties of such complexes over a wide range of temperature to probe the cause of the low magnetic moments. The trend in exchange interaction on substitution of the biguanide moiety has also been studied.

RESULTS AND DISCUSSION

Magnetic data on copper(II) complexes of 2-salicylidenebiguanide (salbg) and its 5-substituted derivatives are given in Tables 1—5. All the complexes except that of 5-Me-salbg have magnetic moments which decrease with decreasing temperature. An attempt was made to fit the experimental data to the Curie–Weiss equation (1). A plot of $1/\chi_a$ against T was linear with definite θ

$$\chi_a = C/(T + \theta) \qquad (1)$$

values for the 5,5-Et_2-, 5-Et-, and 5-Ph-salbg and salbg complexes (Table 6). However, the 5-Me-salbg complex followed the Curie law.

Considering the magnetic moments in these complexes to be due to interactions arising out of polymerisation, the Bleaney-Bowers equation (2) was used to determine

$$\chi_a = \left[\frac{Ng^2\beta^2}{3kT}\cdot\frac{1}{3 + \exp(-J/kT)}\right] + N\alpha \qquad (2)$$

the extent of polymerisation. The average magnetic susceptibilities per copper ion, χ_a', were computed with J, g, and $N\alpha$ as parameters to obtain the best fit. From Tables 1—5 it can be seen that the calculated susceptibilities of the 5-Ph- and 5,5-Et_2-salbg complexes are greater than the experimentally determined ones at high temperature indicating slight departure from the suggested model. A deflection point based on theoretical considerations could not be observed experimentally for the 5-Et-salbg complex. Experimental data for the salbg complex provided an approximate fit to the above equation with $J = -35.18$ cm^{-1} and $g = 1.60$. It is unlikely that the value of g is much less than 2. The model failed completely in the case of the 5-Me-salbg complex.

An attempt was also made to fit the experimental data to the Ising and Heisenberg models.[10] A plot of log $(4k\chi_a T/Ng^2)$ against $1/T$ for the salbg complex gave $g = 1.56$. This indicates absence of any extensive interaction in the linear chain. In all the other cases better values of g were not obtained by the use of this model. A better fit was, however, obtained by use of the Jotham–Kettle

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[9] S. N. Poddar and A. K. Sarkar, *J. Indian Chem. Soc.*, 1968, **45**, 11, 979.

[10] C. G. Barraclough and C. F. Ng., *Trans. Faraday Soc.*, 1964, **60**, 836.

TABLE 1

Magnetic data for the complex of 5,5-Et_2-salbg. $J = -77.4\ cm^{-1}$, $\Delta = 157.8\ cm^{-1}$, $g = 2.19$, $N\alpha = 60 \times 10^{-6}$ c.g.s. units, and $\theta = 50$ °C

T/K	307	280	258	235	210	173	93
$10^6\chi_a$/c.g.s. units (*a*)	1 226.4	1 332.4	1 450.4	1 595.4	1 758.4	2 042.4	3 054.4
(*b*)	1 352	1 463	1 562	1 686	1 841	2 168	3 055
(*c*)	1 224	1 336	1 436	1 537	1 684	2 027	3 028
$\mu_{eff.}$/B.M.	1.736	1.728	1.731	1.733	1.720	1.682	1.508

[a] Experimental data; diamagnetic corrections were made using data from ref. 16. [b] Calculated from the Bleaney-Bowers equation (2). [c] Calculated from the Jotham–Kettle equation (3).

TABLE 2

Magnetic data for the complex of 5-Ph-salbg. $J = -58.4\ cm^{-1}$, $\Delta = 84.8\ cm^{-1}$, $g = 2.19$, $N\alpha = 60 \times 10^{-6}$ c.g.s. units, and $\theta = 15$ °C

T/K	305	283	260	243	210	190	136	118	103	93
$10^6\chi_a$/c.g.s. units (*a*)	1 194.4	1 301.4	1 440.4	1 532.4	1 762.4	1 793.4	2 424.4	2 886.4	3 331.4	3 515.4
(*b*)	1 393	1 488	1 605	1 697	1 924	2 092	2 721	3 019	3 294	3 506
(*c*)	1 217	1 303	1 412	1 504	1 717	1 881	2 524	2 824	3 120	3 358
$\mu_{eff.}$/B.M.	1.706	1.717	1.732	1.727	1.722	1.652	1.625	1.651	1.658	1.617

For Key see Table 1.

TABLE 3

Magnetic data for the complex of salbg. $3J = -478.8\ cm^{-1}$, $g = 2.19$, $N\alpha = 60 \times 10^{-6}$ c.g.s. units, and $\theta = 50$ °C

T/K	305	283	267	255	233	206	163	149	118	93	78
$10^6\chi_a$/c.g.s. units (*a*)	721.6	742.9	785.4	817.5	860.1	902.6	1.084	1 211	1 467	1 616	1 904
(*b*)	721.6	745.2	762.6	779.4	807.8	868.7	1 010.1	1 081	1 316	1 638	1 940
$\mu_{eff.}$/B.M.	1.327	1.297	1.296	1.277	1.267	1.220	1.190	1.201	1.177	1.097	1.091

[a] Experimental data; diamagnetic corrections were made using data from ref. 16. ·Calculated from equation (4).

TABLE 4

Magnetic data for the complex of 5-Me-salbg, $3J = -954.5\ cm^{-1}$, $g = 2.19$, and $N\alpha = 60 \times 10^{-6}$ c.g.s. units

T/K	305	281	275	258	243	233	216	183	153	128	118	98	78
$10^6\chi_a$/c.g.s. units (*a*)	561.5	583.5	605.3	637.8	703.0	735.6	779.1	833.5	1 007.4	1 442.8	1 506.8	1 767.8	2 010.0
(*b*)	560.5	597.0	608.0	639.0	670.0	695.0	742.6	861.9	1 018	1 205	1 302	1 555	1 938
$\mu_{eff.}$/B.M.	1.155	1.147	1.154	1.148	1.169	1.173	1.159	1.05	1.111	1.216	1·193	1.178	1.120

For Key see Table 3.

TABLE 5

Magnetic data for the complex of 5-Et-salbg, $J = -90.40\ cm^{-1}$, $J' = 3.5\ cm^{-1}$, $g = 2.19$, and $N\alpha = 100 \times 10^{-6}$ c.g.s. units

T/K	305	273	249	196	177	160	133	118	103	93
$10^6\chi_a$/c.g.s. units (*a*)	1 191.7	1 213.7	1 313.7	1 537.7	1 560.7	1 582.7	1 660.7	1 694.7	1 761.7	1 806.7
(*b*)	1 241	1 339	1 429	1 636	1 723	1 790	1 880	1 888	1 846	1 752
(*c*)	1 135	1 235	1 346	1 551	1 611	1 724	1 832	1 853	1 824	1 740
(*d*)	1 183	1 272	1 350	1 543	1 628	1 703	1 832	1 913	2 001	2 082
(*e*)	1 142	1 211	1 269	1 406	1 460	1 513	1 612	1 683	1 790	1 889
$\mu_{eff.}$/B.M.	1.706	1.629	1.618	1.553	1.488	1.424	1.330	1.266	1.206	1.160

[a] Experimental data; diamagnetic corrections were made using data from ref. 16. [b] Calculated from the Bleaney-Bowers equation (2) ($2J = -135\ cm^{-1}$). [c] Calculated from the Jotham–Kettle equation (3) ($2J = -135\ cm^{-1}$, $\Delta = 155\ cm^{-1}$). [d] Calculated from equation (5) ($J = -67.8\ cm^{-1}$). [e] Calculated from equation (6) ($J = -90.4\ cm^{-1}$, $J' = 3.5\ cm^{-1}$, $g = 2.19$, $N\alpha =$ 100 c.g.s. units).

TABLE 6

Exchange integrals and Curie and Weiss constants

Ligand	C/c.g.s. units	θ/°C	J/cm^{-1}	Δ/cm^{-1}	g	$10^6N\alpha$/c.g.s. units
5,5-Et_2-salbg	0.4460	50	77.4	157.8	2.19	60
5-Ph-salbg	0.3750	15	58.4	84.8	2.19	60
salbg	0.2481	50	478.8		2.19	60
5-Me-salbg			954.5		2.19	60
5-Et-salbg	0.7144	300	90.4	155	2.19	60

equation (3) [11] for the 5,5-Et_2- and 5-Ph-salbg complexes

$$\chi_a = \left[\frac{Ng^2 \cdot \beta^2}{3\,\boldsymbol{k}T} \cdot \frac{3}{3 + \exp(-J/\boldsymbol{k}T) + \exp(-\Delta/\boldsymbol{k}T)}\right] + N\alpha \quad (3)$$

(Tables 1 and 2). The complexes of salbg and 5-Me-salbg obeyed equation (4) [12] where $-3J$ is the energy separation between doublet and quartet states for a

$$\chi_a = \frac{Ng^2\beta^2}{12\,\boldsymbol{k}T} \cdot \frac{1 + 5\exp(-3\,J/\boldsymbol{k}T)}{1 + \exp(-3\,J/\boldsymbol{k}T)} \quad (4)$$

trinuclear Cu^{II} complex with a closed-chain structure. The results are given in Tables 3 and 4. For the 5-Et-salbg complex a better fit was obtained with equation

$$\chi_a = \left[\frac{Ng^2\beta^2}{12\,\boldsymbol{k}T} \cdot \frac{1 + \exp(-2\,J/\boldsymbol{k}T) + 10\exp(J/\boldsymbol{k}T)}{1 + \exp(-2\,J/\boldsymbol{k}T) + 2\exp(J/\boldsymbol{k}T)}\right] + N\alpha \quad (5)$$

(5)[13] for a trinuclear open-chain structure compared to other models, *viz.* Bleaney-Bowers and Jotham–Kettle. However, the experimental data gave better agreement with values calculated from equation (6) [8] for a distorted

$$\chi_a = \frac{Ng^2\beta^2}{12\,\boldsymbol{k}T} \cdot \frac{\exp(-2\,J/\boldsymbol{k}T) + \exp(-2\,J'/\boldsymbol{k}T) + 10\exp(J/\boldsymbol{k}T)}{\exp(-2\,J/\boldsymbol{k}T) + \exp(-2\,J'/\boldsymbol{k}T) + 2\exp(J/\boldsymbol{k}T)} \quad (6)$$

triangular model where the interactions between atoms Cu^1 and Cu^3 and Cu^1 and Cu^2 are the same but different from that between Cu^2 and Cu^3. The results are in Table 5.

It can thus be concluded that, with the introduction of bulky substituents such as Et, 2Et, and Ph in salbg, distorted trimers and dimers are the probable aggregates whereas salbg and 5-Me-salbg form closed-chain trimers. From this study the complexes can be broadly classified as follows:

Group	Substituent(s) on salbg	Model
(I)	(*a*) 5,5-Et_2 (*b*) 5-Ph	Binuclear
(II)	(*a*) None (*b*) 5-Me	Trinuclear closed chain
(III)	5-Et	Trinuclear distorted triangular

All these complexes have magnetic moments lower than the spin-only value of 1.73 B.M.* The magnetic moments decrease with decreasing temperature except in the case of the methyl derivative. The results indicate the existence of exchange interactions in both the cases. The electronic spectra of all the complexes were recorded (Table 7). The low magnetic moments and high ligand-field band position indicate a distorted square-planar structure. Phenoxide bridges have been assigned to these complexes from a study of their i.r. spectra (Table 8).

TABLE 7

Electronic spectral data *

Ligand										
5,5-Et_2-salbg	1 075	985	775	600	400	365	315	300		250
	(9 303)	(10 150)	(12 900)	(16 660)	(25 000)	(27 400)	(31,750)	(33 340)		(40 000)
5-Ph-salbg	1 085	975	775	590	390		325	290		250
	(9 217)	(10 260)	(12 900)	(16 940)	(25 640)		(30 770)	(34 470)		(40 000)
salbg	975	910	785	635	425	375	335	285	265	237
	(10 260)	(10,990)	(12 740)	(15 750)	(23 530)	(26 670)	(29 850)	(35 100)	(37 740)	(42 220)
5-Me-salbg	975	910	800	685	425	385	325	300	265	235
	(10 260)	(10 990)	(12 500)	(14,600)	(23 530)	(25 970)	(30 770)	(33 340)	(37 740)	(42 550)
5-Et-salbg	1 090	980	865	670	440	360	335	275		235
	(9 175)	(10 210)	(11 560)	(14 920)	(22 730)	(27 770)	(29 850)	(30 370)		(42 550)

* Wavelength in nm with absorption coefficients (ε/l mol^{-1} cm^{-1}) in parentheses.

Group (I) *Complexes*.—The data in Tables 1 and 2 show a better fit of the experimental values to the Jotham–Kettle model. This indicates pairing of bonding electrons in the same metal orbital due to thermal population of a low-lying spin-singlet state which was not considered in the Bleaney-Bowers model.

TABLE 8

I.r. spectral data (cm^{-1})

Ligand	ν(M–N)	Phenoxide bridge stretching
5,5-Et_2-salbg	3 300	1 572
5-Ph-salbg	3 340	1 580
salbg	3 330	1 597
5-Me-salbg	3 355	1 585
5-Et-salbg	3 330	1 597

The electronic spectra (Figure 1) of the complexes in the ligand-field region are very similar to those of [Cu(salen)]·CuX_2 complexes [salen = *NN*′-ethylenebis(salicylideneiminato)].[7] Higher ligand-field band posi-

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* 1B.M. ≈ 9.27×10^{-24} A m^2.

[11] R. W. Jotham and S. F. A. Kettle, *Inorg. Chem.*, 1970, **6**, 1390.

[12] A. P. Ginsberg, R. C. Sherwood, and E. Koubeck, *J. Inorg. Nuclear Chem.*, 1967, **29**, 357.

[13] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, 1968, **49**, 2183.

tions of the complexes indicate distorted square-planar geometry; most of the bands are weak in nature. In the u.v. region (Table 7) a band at 335—315 nm is due to the salicylaldehyde part of the ligand. Bands in the range 285—300 nm are due to charge-transfer metal–ligand interaction. The band at 250 nm is due to the metal–biguanide chromophore.[14] In the complex of salbg this band occurs at 230 nm. The red shift can be interpreted as due to greater delocalisation of π electrons in the system.

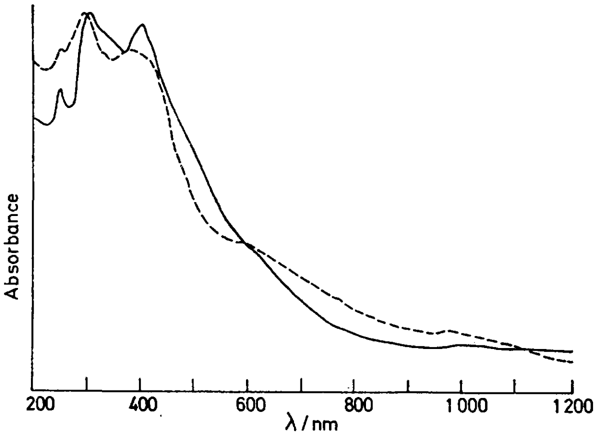
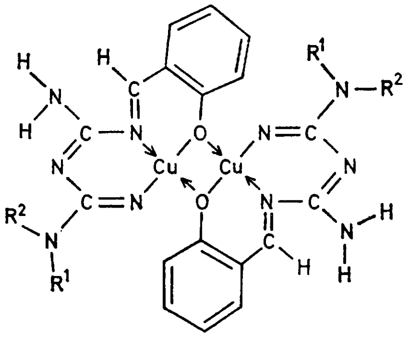


FIGURE 1 Electronic spectra of the 5,5-Et$_2$-salbg (——) and 5-Ph-salbg complexes (— — —)

The absence of a band at 1 540 cm^{-1} (phenoxide stretching before bridging) in the i.r. spectra (Table 8), but the presence of bands in the region 1 572—1 580 cm^{-1}, indicates phenoxide bridging in the complexes.[15] The shift of this band to a higher frequency is probably due to the increase in C–O bond strength for extended delocalisation of the π system of the biguanide moiety.

On the basis of the above studies, structure (A) is proposed for this series of complexes.



(A)

Group (II) *Complexes*.—For the complex of salbg ($\mu_{\text{eff.}}$ 1.33 B.M.) the magnetic moment decreases with decreasing temperature indicating exchange interaction. It remains constant, however, in the case of the 5-Me-salbg complex. In spite of the presence of exchange interaction, the constancy of the magnetic moment with temperature is due to attaining the minimum value of magnetic moment, $\mu_{\text{eff.}} = \{\frac{1}{3}[0^2 + 0^2 + (1.73)^2]\}^{\frac{1}{2}} = 1$ B.M., for a trinuclear Cu$^{\text{II}}$ complex with a closed-chain structure. This value is attained by the salbg complex at liquid-air temperature only.

In this group, the lowest magnetic moments and highest ligand-field band positions (Figure 2) compared to the other complexes studied suggest the least distortion from square planarity. The absence of a band at 1 540 cm^{-1} in the i.r. spectra (Table 8) but the presence of bands at 1 585—1 567 cm^{-1} clearly supports the assumption of phenoxide bridging in the complexes. The increase in energy of these bands over the reported value[15] of 1 560 cm^{-1} may be attributed to the delocalised π system[14] of the biguanide moiety.

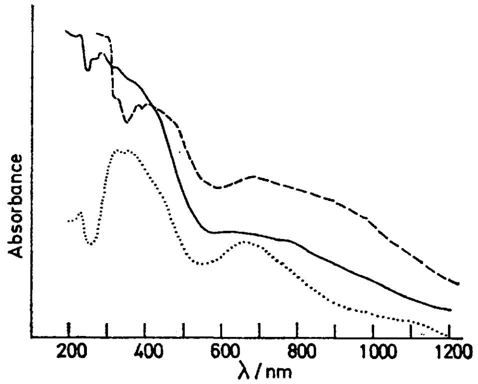
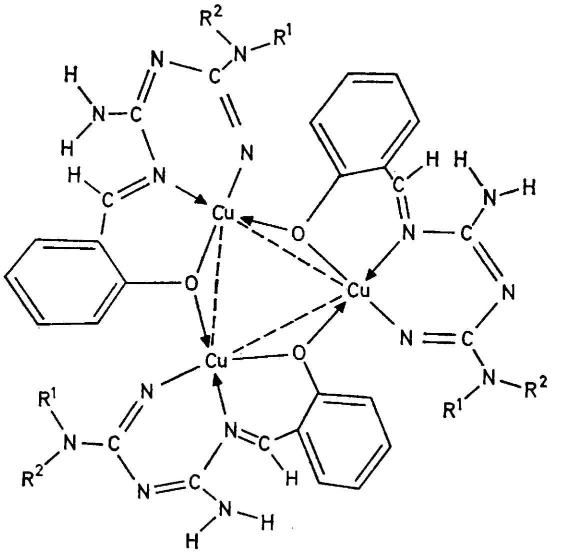


FIGURE 2 Electronic spectra of the salbg (——), 5-Me-salbg (— — —), and 5-Et-salbg complexes (· · · ·)

The above findings can be explained by assuming structure (B).



(B)

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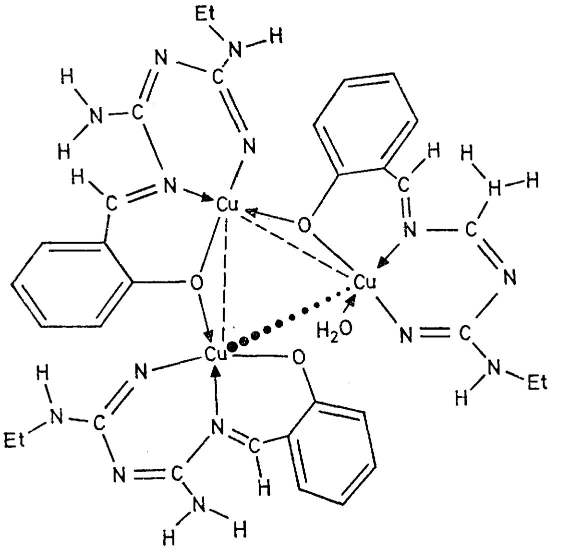
[14] D. Sen, *J. Chem. Soc.* (*A*), 1969, 2900.

[15] C. M. Harris and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2723.

[16] B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.

Group (III) *Complex*.—The magnetic moments of the 5-Et-salbg complex conform more to a distorted triangular model (Table 5). The ligand-field spectra show a similarity to those of Group (I) complexes. The distorted triangular structure requires a terminal water molecule as in (C). Due to a number of bands in the region 3 400—3 300 cm^{-1}, the presence of a water molecule in the complex could not be confirmed. The complex has band positions in the u.v. and visible region similar to those of groups (I) and (II), revealing distorted square-planar geometry. The absence of a band at 1 540 cm^{-1} in the i.r. spectrum but the presence of bands at 1 585—1 567 cm^{-1} clearly indicates phenoxide bridging.



(C)

EXPERIMENTAL

The complexes were prepared by the methods described by Poddar and Sarkar.[9]

	Analyses/%			
	Found		Calc.	
Ligand	Cu	N	Cu	N
5-Ph-salbg	18.2	20.2	18.5	20.35
5,5-Et$_2$-salbg	19.65	21.8	19.9	21.9
5-Me-salbg	22.3	24.8	22.5	24.8
salbg	24.7	26.4	24.9	26.6
5-Et-salbg	22.5	23.8	21.8	24.0

Spectra in the range 200—1 200 nm were recorded on a Cary 14 spectrophotometer, and i.r. spectra (625—4 000 cm^{-1}) were obtained on a Perkin-Elmer 237B spectrophotometer from Nujol mulls. Magnetic measurements were made on a Gouy balance with a low-temperature cryostat placed between the poles of the magnet; the Gouy tube was completely enclosed by the cryostat. The whole measuring system was enclosed in an air-tight moisture-free chamber. The measurements were made at least twice and the sample was prepared separately for each experiment. The variation in the results was within 1%.

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