

Tetranuclear bimetallic complexes of cobalt (II) and copper (II) with biacetylazinedihydrazone

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Binuclear cobalt (II) complexes of biacetylazinedihydrazone (BAADH), $\text{Co}_2(\text{BAADH})_2\text{X}_4$ ($\text{X} = \text{Cl}^-$, Br^- , SCN^- , NO_3^-) react with copper (II) halides to give tetranuclear bimetallic complexes $[\text{Co}(\text{BAADH})_2\text{X}_4][\text{CuY}_2]_2$ ($\text{Y} = \text{Cl}^-$, Br^-). IR and electronic spectra point to the presence of chromophores (CoN_4X_2) and (CuN_2Y_2) implying coordination of terminal NH_2 groups of BAADH with copper (II). Electrochemical reduction of each complex occurs in two steps. The first step is a two-electron transfer process where each terminal copper (II) is transformed to copper (I) state. The more cathodic second step involves one electron where only one of the two inner core cobalt (II) ions is reduced to cobalt (I) state. The redox pattern is supported by additional evidence gathered from similar investigations on the linear trimeric $[\text{Cu}(\text{DMG})_2]$ (CuCl_2)₂ species (DMG = dimethylglyoximate ion) and related species.

Multinuclear metal complexes have attracted much attention¹⁻⁵ in recent years. Dimeric structure of copper (II) acetate, trimeric nickel (II) and tetrameric cobalt (II) acetylacetonate complexes, and the related tetrameric cubane type complexes of cobalt (II) and nickel (II)⁶⁻⁸, trimeric copper (II) complexes with pyridine-2-carbaldoxime^{9,10}, dinuclear complexes of phthalazine type of ligands^{11,12}, homo- and hetero-multinuclear complexes derived from schiff bases^{13,16}, imino-alcohols^{17,18} and polyketones¹⁸⁻²² and several azine and oximate as well as related complexes²³⁻²⁶ are some of the representative complexes in this field. Besides, binuclear macrocyclic complexes constitute a frontier area of current research²⁷⁻²⁹.

The binuclear metal complexes of 3,6-dimethyl-2,7-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone (BAADH)^{23,24} were considered promising starting materials to prepare homo- and hetero-tetranuclear metal complexes of BAADH. In the present study we have succeeded in isolating tetranuclear dicobalt (II) and dicopper (II) complexes of this ligand. The complexes can be termed as tetranuclear bimetallic complexes because two kinds of metal ions can be placed in two different ordered arrangements. A pair of cobalt (II) ions, in the inner core of the complex, binds the BAADH moieties in an anti-configuration projecting the terminal NH_2 groups in appropriate positions for further coordination with copper (II) ions. Electron transfer reactions of these complexes have been also studied with the objective of furthering our understanding of hetero multinuclear systems.

Materials and Methods

Copper (II) chloride dihydrate was a BDH reagent and copper (II) bromide was prepared by the literature method³⁰. The ligand BAADH was prepared as reported earlier²⁴. The tetrathiocyanato/tetrahalo and tetranitrato-bis-(3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone) dicobalt (II) complexes, $\text{Co}_2(\text{BAADH})_2\text{X}_4$, were prepared as described earlier²⁴.

All the tetranuclear bimetallic complexes were synthesized following similar procedures and a typical preparation is described here.

Tetranitrato-bis-(3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone) dicobalt (II) tetrachlorodicopper (II) [$\text{Co}_2(\text{BAADH})_2(\text{NO}_3)_4(\text{CuCl}_2)_2$]

A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.0 g; 0.012 mol) in 20-30 ml of methanol was added to $\text{Co}_2(\text{BAADH})_2(\text{NO}_3)_4$ (3.8 g; 0.005 mol) in 50 ml of methanol when the colour changed rapidly from orange yellow to yellowish green. After a few minutes, the resulting yellowish green product was filtered, washed with methanol followed by ether and dried *in vacuo*. Copper (II) was estimated iodometrically and cobalt (II) was estimated by oxinate method after removal of copper (II) as sulphide.

Analytical data of the complexes are recorded in Table 1.

Results and Discussion

The tetrahalo-, tetrathiocyanato- and tetranitrato-bis-(BAADH)-dicobalt (II) complexes act with co-

Table 1—Colour and analytical data of the Co(II)-Cu(II) hetero bimetallic tetranuclear complexes

S. No.	Complexes	Colour	Found (Calc.), %			
			Cobalt	Copper	Halide	N
1	[Co ₂ (BAADH) ₂ (Cl ₄)(CuCl ₂) ₂]	Dark brown	12.36 (12.82)	13.5 (13.69)	30.3 (30.86)	17.92 (18.26)
2	[Co ₂ (BAADH) ₂ (Br ₄)(CuBr ₂) ₂]	Chocolate brown	9.58 (9.24)	9.92 (9.87)	50.8 (51.7)	12.73 (13.1)
3	[Co ₂ (BAADH) ₂ (NO ₃) ₄ (CuCl ₂) ₂]	Yellowish green	11.1 (11.5)	12.4 (12.28)	13.5 (13.84)	21.7 (21.83)
4	[Co ₂ (BAADH) ₂ (NO ₃) ₄ (CuBr ₂) ₂]	Yellowish brown	10.1 (9.8)	10.4 (10.46)	26.1 (26.57)	18.48 (18.6)
5	[Co ₂ (BAADH) ₂ (SCN) ₄ (CuCl ₂) ₂]	Yellowish grey	10.98 (11.68)	12.53 (12.47)	13.86 (14.05)	21.1 (21.17)
					7.7* (7.89)	

*S value

Table 2—Magnetic and electronic spectral data of the Co(II)-Cu(II) hetero bimetallic tetranuclear complexes

Complexes (No. as in Table 1)	μ_{eff} (B.M.)	λ_{max} (cm ⁻¹)
1	6.03	8,400; 15,200; 23,300 sh; 30,300
2	6.06	8,300; 16,700 (as); 23,500; 30,800.
3	6.19	8,300; 16,200; 23,300; 30,200.
4	6.24	8,300; 15,800; 21,200; 30,200.
5	6.06	8,400; 15,400; 19,600; 30,800.

nsiderable ease as coordinating ligands through their terminal NH₂ groups with CuCl₂ or CuBr₂ to give tetranuclear bimetallic complexes. Complex formation is completed within a few minutes and partial metal ion exclusion, i.e., replacement of cobalt (II) ions by copper (II) ions takes place when the reaction is either carried out over a long period or copper (II) ions are added in large excess.

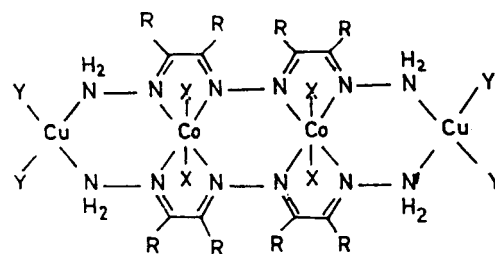
Infrared spectra

The IR spectra of tetranuclear bimetallic complexes resemble one another but differ from those of the parent BAADH complexes in respect of NH₂ stretching vibrations in the region 3300-3000 cm⁻¹. The ν_{as} and ν_{s} modes of NH₂ vibrations are lowered by 60-100 cm⁻¹ in tetranuclear complexes compared to the positions in the parent complexes. This lowering is due to decrease in electron density in the N-H bonds due to coordination with copper (II) ions. This $\nu_{\text{C}} \cdots \text{N}$ mode in the tetranuclear complexes is also lowered due to charge withdrawal arising from coordination of copper (II) to the -NH₂ groups.

For the tetrathiocyanate complex a band is observed at ~ 2100 cm⁻¹ implying coordination of SCN⁻ group through its nitrogen atom. In nitrate complexes, the coordination of NO₃⁻ ion through one of its oxygen atoms³¹ is indicated by the appearance of a pair of characteristic bands at ~ 1400 and ~ 1265 cm⁻¹ which is further supported by the presence of a third band at ~ 1025 cm⁻¹. These spectral features suggest tetranuclear bimetallic structures (I). However, the complexes can also exist in a more involved polymeric structure (II), particularly in the solid state, since such structure are easily adopted by copper (II) in similar chemical environment such as dichloro-bis-(ethylenediamine) copper (II).

Magnetic moments and electronic spectra

The magnetic susceptibility values at room temperature for the tetranuclear bimetallic complexes lie in

R = CH₃X = Cl⁻, Br⁻, NO₃⁻, SCN⁻Y = Cl⁻, Br⁻

[I]

Table 3—Polarographic data of the Co(II)-Cu(II) hetero bimetallic tetranuclear complexes in aqueous DMF

Complexes (No. as in Table 1)	First Wave			Second Wave		
	$-E_{1/2}$ (V vs. SEC)	Slope $^{-1}$ (mV)	i_d (μ A)	$-E_{1/2}$ (V vs SCE)	Slope $^{-1}$ (mV)	i_d (μ A)
1	0.4	83	4.1	1.66	96	2.3
2	0.38	79	4.8	1.64	86	2.9
3	0.4	89	4.4	1.43	65	2.4
4	0.36	85	4.2	1.44	82	2.9
5	0.46	82	3.9	1.42	97	2.1

the range $14,000\text{--}15,000 \times 10^{-6}$ e.g.s. units per mole with magnetic moments varying from 6.03 to 6.24 B.M. (Table 2). The data could not be compared with those for any hetero-nuclear complex containing cobalt (II) and copper (II) in the mole ratio 1:1. However, comparison of the magnetic data of the present complexes with those of several well established magnetically concentrated homo- and hetero-nuclear complexes containing three to four metal atoms and five to eight unpaired electrons^{32–35} indicated that the present complexes contain cobalt (II) ions in spin-free states though the observed susceptibility values are relatively lower than the theoretically expected spin-only susceptibilities. Low values of susceptibility are, however, not unexpected. The conjugated system of the ligand BAADH is a powerful pathway for magnetic exchange interactions through antiferromagnetic spin coupling or through the halogen bridge between two copper ions as in structure (II).

Electronic spectra of the complexes measured in solid state are consistent with magnetic data (Table 2) and exhibit features that arise due to ligand field bands of Cu(II) and Co(II) ions in $^2B_{1g}$ and $^4T_{1g}$ ground states respectively. All of these complexes show a broad band near $15,000 \text{ cm}^{-1}$ which resembles the general environment³⁶. The asymmetry and width of this band characterize low symmetry ligand field around the copper (II) ion with Jahn-Teller distortion. The electronic spectra of a series of complexes each containing three cobalt (III) ions and one copper (II) ion have been reported^{17,18}. In these complexes a band located in the range $13,000\text{--}15,000 \text{ cm}^{-1}$ is assigned

chiefly to the $^2B_{1g} \rightarrow ^2E_{1g}$ transition of copper (II) ions¹⁷.

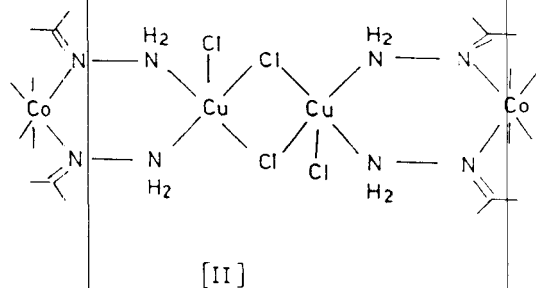
Usually, cobalt (II) complexes show^{37,38} a band near $16,000 \text{ cm}^{-1}$ due to the transition $^4T_{1g} \rightarrow ^4A_{2g}$. For the present series of complexes this transition possibly overlaps with Cu(II) transitions and further resolution has not been possible. In the lower frequency region all these complexes show a weak band near 8000 cm^{-1} which can be attributed to $^4T_{1g} \rightarrow ^4T_{2g}$ transition for cobalt (II) ion in an octahedral field. In the higher frequency region the spectra are not well resolved; but for other complexes a fairly intense band appears near $23,000 \text{ cm}^{-1}$. This band has been assigned to the transition $^4T_{1g} \rightarrow ^4T_{1g}(P)$. The intensity of this band indicates considerable charge-transfer associated with this transition or some intensity stealing from the neighbouring higher intensity band at $\sim 30,000 \text{ cm}^{-1}$.

Electrochemical studies

Polarographic data show (Table 3) two well-defined redox waves for each complex with $E_{1/2}$ values in the ranges -0.36 to -0.4 V and -1.4 V to -1.6 V . The former redox process is accompanied by two-electron transfer while the later is associated with one-electron transfer. Literature recorded³⁹ $E_{1/2}$ values for a number of complexes show that cobalt (II) is reduced in the range -0.4 V to -1.4 V and copper (II) in the range -0.2 to -1.4 V .

The $E_{1/2}$ values and the number of electrons transferred in two successive steps for the tetranuclear bimetallic complexes show that the redox processes are predominantly metal based. The most probable pathway for the redox processes is given in Scheme 1. In the first step, the terminal copper (II) ions are reduced to copper (I) and in the second stage, one of the cobalt (II) ions in the inner-core is reduced to cobalt (I).

The suggested pathway for reduction is supported by the reported electrochemical behaviour of the trinuclear copper (II) complex, $[\text{Cu}(\text{DMG})_2](\text{CuCl}_2)_2$ (where DMG is dimethyl glyoximate ion)²⁶. This trimer has close structural analogy with the present ser-



ies of complexes having the chromophores CuN_4 and CuO_2Cl_2 . The linear trimer is reduced quasi-reversibly in a two-electron step at a substantially low cathodic potential ($E_{1/2} = -0.26$ V) and no other wave appears upto -1.3 V beyond which an ill-defined wave is observed. The results indicate that each terminal copper (II) ion is reduced to copper (I) state in the two-electron transfer step. Triangular copper (II) complexes $[\text{Cu}_3(\text{HPL})_3\text{OH}]^{2+}$ (where HPL = pyridine-2-carbaldoxime) have been reported^{40,41} to undergo one-electron reduction at -0.3 to -0.45 V, stabilising the complex with metal ions in ambivalent oxidation states of $+1$ and $+2$. The $E_{1/2}$ values of these complexes are found to coincide closely with the $E_{1/2}$ values observed in the first step of reduction of the present tetranuclear bimetallic complexes. The copper (II) ions in the aforesaid trimers and those in the present tetranuclear species have similar ligand environments. Thus, the structural factors as well as the $E_{1/2}$ values imply transfer of electrons to the copper centres in the first step of reduction of the tetranuclear bimetallic species.

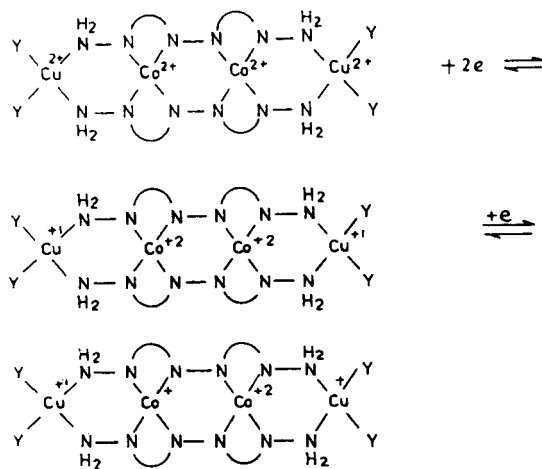
Besides, electrochemical behaviour of other hetero-nuclear metal complexes is also found to exhibit a similar pattern. The redox behaviour of $[\text{Ni}(\text{DtO})_2(\text{SnX}_4)_{1,2}]^{2-}$ (DtO = dithiooxalate, $\text{X} = \text{Cl}^-$, F^- , Br^- , I^-)⁴² and rhena-acetylacetonate complexes⁴³ $[\text{cis}-(\text{OC})_4\text{Re}(\text{CH}_3\text{CO}.\text{CH}_2.\text{COCH}_3)_2]_n\text{M}$ (where $\text{M} = \text{Fe(III)}$, $n = 3$; $\text{M} = \text{Cr(III)}$, $n = 3$ or $\text{M} = \text{Cu(II)}$, $n = 2$) evince that the first redox process preferentially concerns the terminal metal ions M rather than the inner-core metal centres. The redox reaction of the tetranuclear bimetallic complexes on the whole supports the mechanism suggested in Scheme 1.

The second step of reduction is appreciably cathodic and $E_{1/2}$ values are found to lie near -1.5 V (Table 3). This step involves the reduction of one of the inner-

-core cobalt (II) ions to cobalt (I) state. The high cathodic $E_{1/2}$ values and stabilization of cobalt ions in ambivalent states in the tetranuclear bimetallic complexes are due to metallo-bridged thermodynamically stable macrocyclic structure [1].

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