

Metal Complexes as Ligands: Trinuclear Alkali Metal Complexes with Copper(II) Acetylacetonate

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A report on preparation and characterization of some new complexes of the general formula $[Cu(ac-ac)_2(ML)_2]$, has been presented here

M = Li, Na or K;

L = Deprortonated picolinic acid, salicylic acid, acetyl acetone, *o*-nitrobenzoic acid

acac = Acetylacetone -

INTRODUCTION

The study of the coordination chemistry of alkali metal is interesting due to its possible role in plant metabolism, desalination of sea water and to understand its transport mechanism from soil to plant. This wonderful field remained unexplored and neglected till recently. Because of the nature of alkali metal complexes no d-d transition, no magnetic properties, instability to solution, very little work has been done either to investigate the few known compounds or to prepare new ones. However, the work has been extended to use transition metal complexes as ligand, in which magnetic property and absorption spectra have been considered to justify the alkali metal complexes.

The formation of oxygen bridged binuclear complexes from copper salicylaldimine has been well established by previous workers. In view of the above information, it was decided to extend the investigation by a synthetic application of the complexes of $Cu(acac)_2$ with alkali metal salts.

The complexes of alkali metals known so far, are usually decomposed by water. Therefore, most of the work has been carried out in non-aqueous solvents.

EXPERIMENTAL

Preparation of Complexes

The formation of $Cu(acac)_2$ has well been established.¹⁻³ Our usual method of

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synthesis was to take $\text{Cu}(\text{acac})_2$ in a mixture of benzene and absolute ethanol and alkali metal salts were added to it in the ratio of 1 : 2. It was refluxed with constant stirring in hot plate for about 1–2 h. Finally, the adducts were precipitated in hot condition.

The results of elemental and physical data of the complexes are given in Table 1.

TABLE 1

Compound	Colour	Analysis % : Found/Calcd				Decomp. temp (°C)	μ_{eff} (BM)
		C	H	N	Cu		
$\text{Cu}(\text{acac})_2$	Blue	—	—	—	—	240	2.1
$\text{Cu}(\text{acac})_2$ (Li PreA) ₂	Brownish yellow	51.21 (50.81)	4.56 (4.29)	5.62 (5.38)	12.12 (12.22)	265	2.2
$\text{Cu}(\text{acac})_2$ (Na PreA) ₂	Brown	47.38 (47.86)	4.21 (3.98)	5.22 (5.07)	11.23 (11.51)	260	2.2
$\text{Cu}(\text{acac})_2$ (K PreA) ₂	Brown	45.35 (45.24)	3.89 (3.77)	4.69 (4.79)	10.23 (10.8)	263	2.1
$\text{Cu}(\text{acac})_2$ (Li ONBA) ₂	Brown	47.43 (47.41)	3.88 (3.42)	4.72 (4.61)	10.30 (10.54)	217	2.3
$\text{Cu}(\text{acac})_2$ (Na ONBA) ₂	Brown	45.06 (45.03)	3.68 (3.44)	4.36 (4.37)	9.32 (9.92)	265	2.1
$\text{Cu}(\text{acac})_2$ (K ONBA) ₂	Brown	42.92 (42.88)	3.26 (3.27)	4.28 (4.16)	9.42 (9.45)	213	2.2
$\text{Cu}(\text{acac})_2$ (Li SalA) ₂	Brownish yellow	52.21 (52.41)	4.84 (4.36)	—	11.45 (11.55)	260	2.2
$\text{Cu}(\text{acac})_2$ (Na SalA) ₂	Brownish yellow	49.51 (49.52)	4.68 (4.12)	—	10.86 (10.90)	262	2.2
$\text{Cu}(\text{acac})_2$ (K SalA) ₂	Brown	46.82 (46.94)	4.11 (3.91)	—	10.21 (10.35)	264	2.1

RESULTS AND DISCUSSION

The high decomposition temperatures of these adducts, compared to that of $\text{Cu}(\text{acac})_2$, show the strong bonding, probably through oxygen atoms of complex ligands to the alkali metals.

Magnetic measurements were taken on cation Faraday electronic balance at 27°C. The magnetic moment of $\text{Cu}(\text{acac})_2$ is 2.1 (B.M.) and suggested a square planer structure, while the magnetic moments of adducts are also in between 2.1 to 2.3 B.M. Therefore, the stereochemistry of $\text{Cu}(\text{acac})_2$ unit in alkali metal complex compounds almost remains same. Hence it suggests that alkali metals are coordinated through the oxygen atoms of the ligands $[\text{Cu}(\text{acac})_2]$.

The adducts are characterized by observing the C—O stretching frequency in IR spectra metal complex ligands and the alkali metal complexes.⁴⁻⁹

Infrared spectra measurements were made in Nujol Mull for the ligands and complexed between 4000–650 cm^{-1} . Selected absorption bands in different regions are given in Table 2.

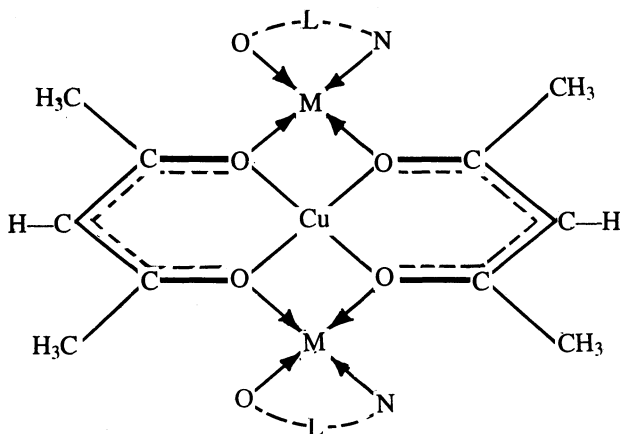
TABLE 2

Compounds	Frequency (cm^{-1})		
$\text{Cu}(\text{acac})_2$	1577	1552	1529
$\text{Cu}(\text{acac})_2(\text{Li PreA})_2$	1590	1505	1520
$\text{Cu}(\text{acac})_2(\text{Na PreA})_2$	1595	1540	1520
$\text{Cu}(\text{acac})_2(\text{K PreA})_2$	1590		
$\text{Cu}(\text{acac})_2(\text{Li ONBA})_2$	1590		
$\text{Cu}(\text{acac})_2(\text{Na ONBA})_2$	1590		
$\text{Cu}(\text{acac})_2(\text{K ONBA})_2$	1595		
$\text{Cu}(\text{acac})_2(\text{Li SalA})_2$	1592		
$\text{Cu}(\text{acac})_2(\text{Na SalA})_2$	1590		
$\text{Cu}(\text{acac})_2(\text{K SalA})_2$	1590		

It has been generalised that metal acetyl acetonates, when they are monomeric, the C=O frequency is below 1580 cm^{-1} whereas, when it is a polymer with oxygen bridges, the C—O frequency splits into two, one above 1580 cm^{-1} due to bridging and the other below 1580 cm^{-1} (normal).

In these polynuclear alkali metal copper(II) acetyl acetonates, the C—O frequencies have been observed not to be in their normal range, but invariably higher between 1580–1600 cm^{-1} . This is quite suggestive that all these oxygens are bridged ones, bridging the copper metal and most probably the alkali metal¹⁰⁻¹⁴.

From magnetic properties and I.R. spectra of the adducts, it is clear that the bonding between $\text{Cu}(\text{acac})_2$ and alkali metal salts is most likely through oxygen atoms of carbonyl group. The structure and bonding of the newly prepared compounds corresponding to the general formula $[\text{Cu}(\text{acac})_2(\text{ML})_2]$ is shown on next page.



REFERENCES

1. G.T. Morgan and H.W. Moss, *J. Chem. Soc.*; **105**, 189 (1914).
2. L.J. Ballomy and R.F. Broch, *J. Chem. Soc.*, 491 (1954).
3. K. Nakamoto, P.J. McCarthy and A.E. Martall, *J. Am. Chem. Soc.*, **83**, 1272 (1961).
4. A. Grun and E. Boedeokar, *Baz.*, **43**, 1051 (1910).
5. Ph.D. Thesis of Kolombos, University College, London (1970).
6. H. Diehl, *Ram. Rev.*, **21**, 39 (1937).
7. J. Lecomte, *Disc. Faraday Soc.*, **2**, 125 (1950).
8. C. Dural, R. Fareymann and J. Leeomla, *Bull. Soc. Chem.*, **19**, 106 (1952).
9. L.J. Ballamy, G.S. Spacer and J.D.H. Strokland, *J. Chem. Soc.*, 4653 (1952).
10. D.M. Sigorin, *Ser. Akad. Nauk. SSSR Fiz. Zh. Khim.*, **17**, 196 (1953).
11. H.W. Morgen, U.S. Atomic Energy Commission Report AFCD, 2659 (1949).
12. M. Calvin and K.W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
13. E.A. Suggam, *Dokl. Akad. Nauk. SSSR*, **81**, 853 (1951).
14. J.M. Robartsin, *J. Chem. Soc.*, 1222 (1951).

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