1120. *Adducts of Bistrifluoroacetylacetonatocopper*(II) *and the Thermochromism of Bis-β-diketonatocopper*(II) *Species.*

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The formation of adducts of bistrifluoroacetylacetonatocopper(II) with various donor molecules has been examined; a marked preference for sexico-ordination as opposed to quinqueco-ordination is shown. The blue-green thermochromism of both bisacetylacetonatocopper(II) and the trifluoroacetylacetonato-analogue is shown to be due to thermal broadening of the first allowed electronic transition.

The formation of quinqueco-ordinate adducts of square-planar bis-β-diketonatocopper(II) complexes with heterocyclic bases has been described.[1] Since copper(II) complexes of fluorinated β-diketones are known,[2,3] we have examined the influence of electron-withdrawal by fluorine atoms in the ligand on the nature of the adducts of a copper complex of this type.

Although the unfluorinated complex bisacetylacetonatocopper(II) adds only one molecule of bases such as pyridine or quinoline,[1] by contrast, bistrifluoroacetylacetonatocopper(II), $Cu(TFacac)_2$, readily adds two molecules of base. A 1 : 1 adduct of pyridine with the complex can also be obtained, however; this is similar to the analogue $Cu(acac)_2py$ except that the pyridine is more firmly held. Although 1 : 1 and 1 : 2 adducts have been isolated previously in a few cases,[1a] it was held that the second molecule of base was merely occupying sites in the crystal lattice and was not bound to the copper atom. Now, in view of the great tendency of the copper atom in $Cu(TFacac)_2$ to become sexico-ordinate, through solvation if necessary, it appears likely that both molecules of base in $Cu(TFacac)_2$,2Base are co-ordinated, particularly in view of the single peaks in the infra-red spectra observed for vibrations of the pyridine molecules, suggesting that both are in the same environment. The electronic spectra of the planar complex $Cu(TFacac)_2$, the quinqueco-ordinate $Cu(TFacac)_2$ monopyridine, and the octahedral $Cu(TFacac)_2$ bispyridine are different, establishing that the 1 : 1 and 1 : 2 adducts are different compounds and that the pyridine is not merely trapped in the lattice.

It was pointed out,[4] many years ago, that compounds of the type bis-β-diketonatometal(II) form stable addition compounds with two donor molecules, and we have found that this is true of the fluoro-complex $Cu(TFacac)_2$, which readily combines with such salts as tetramethylammonium chloride, but only in donor solvents such as ethanol. We have isolated the green tetramethylammonium chloro(bistrifluoroacetylacetonato)ethanolcuprate(II), $[(CH_3)_4N][Cu(TFacac)_2(C_2H_5{\cdot}OH)Cl]$, from which the ethanol cannot be removed without decomposition. The stability of such salts varies with the added components; the compound from tetramethylammonium chloride may be kept in a sealed tube indefinitely, while the sole iodo-compound obtained, green triphenylmethylphosphonium iodo(bistrifluoroacetylacetonato)ethanolcuprate(II), decomposed completely to the parents,

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[1] (*a*) Graddon and Walton, *J. Inorg. Nuclear Chem.*, 1961, **21**, 49; (*b*) Gillard and Wilkinson, *J.*, 1963, 5399.

[2] Belford, Martell, and Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

[3] Fackler, Cotton, and Barnum, *Inorg. Chem.*, 1963, **2**, 97.

[4] Morgan and Moss, *J.*, 1914, **105**, 189.

$Cu(TFacac)_2$ and triphenylmethylphosphonium iodide, within ten minutes at room temperature. The infrared spectra of these salts are consistent with sexico-ordination; in particular, the absence of absorption due to free carbonyl shows that the diketonate chelate rings remain closed.

The formation of unstable ethanolates of the complex $Cu(TFacac)_2$ itself was mentioned[2] some years ago. We have confirmed that when this complex is crystallised from ethanol at −10°, a Cambridge-blue solvate is obtained, but this loses ethanol very readily even at 0° and could not be characterised. However, the royal-blue solvate obtained from acetone under similar conditions was found to be a 1 : 1 adduct which readily lost acetone to form the original material $Cu(TFacac)_2$. This acetone solvate presumably contains quinqueco-ordinated copper(II), one of the few compounds containing the bistrifluoroacetylacetonatocopper(II) grouping of which this is true.

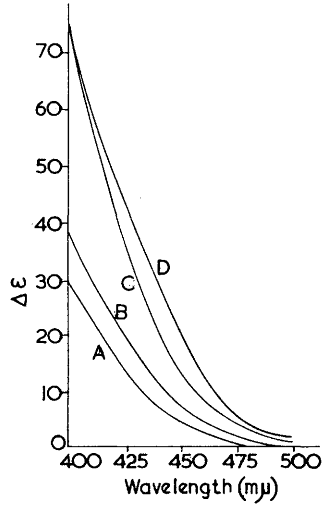

FIG. 1. Effect of temperature on band III of bisacetylacetonatocopper(II). A, $\varepsilon_{32} - \varepsilon_{20}$; B, $\varepsilon_{40} - \varepsilon_{20}$; C, $\varepsilon_{60} - \varepsilon_{20}$; D, $\varepsilon_{75} - \varepsilon_{20}$.

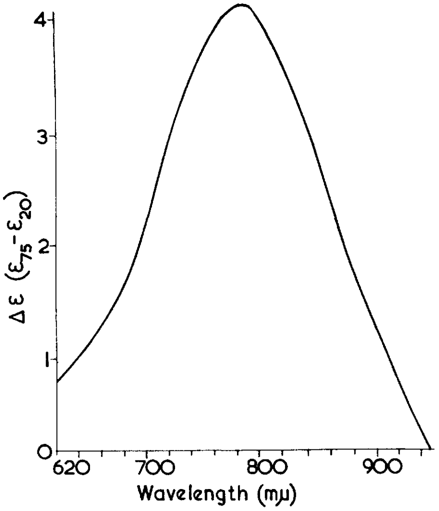

FIG. 2. Effect of temperature on band V of bisacetylacetonatocopper(II).

While the crystalline complex $Cu(TFacac)_2$ is slate-blue at all temperatures up to its melting point, the molten material is deep green. It is possible that, in the melt, the lattice collapses, allowing association to occur and thus giving each copper atom a higher co-ordination number than in the crystal. If this is so, the energy of association is not great, for the compound sublimes readily at 140°. A more likely explanation is that the compound shows thermochromism, particularly in view of the marked reversible colour changes we have observed on heating solutions of the compound in xylene, chlorobenzene, or benzene; the royal-blue cold solutions become green on boiling. The same changes are readily observed in solutions of bisacetylacetonatocopper(II) itself. Association certainly does not occur in boiling benzene or chlorobenzene: the molecular weights, determined ebullioscopically, show that both bisacetylacetonatocopper(II) and bistrifluoroacetylacetonatocopper(II) are monomeric under these conditions in both solvents.

The thermochromism in the visible region of both complexes $Cu(acac)_2$ and $Cu(TFacac)_2$ is associated with the first allowed electronic absorption band (band III in the notation of a recent paper;[3] it occurs at ~300 mμ, and was assigned as $\pi_4^* \longleftarrow \pi_3$). At raised temperatures, band III broadens; this broadening is caused by the alteration with temperature of the relative populations of lower vibrational levels of the ground state. Beer's law is obeyed at 60° (at 440 and 700 mμ) in both cases, showing that no change in the species present has occurred, and therefore that the thermochromism is a property of the monomeric bis-β-diketonatocopper(II) molecules. It may be deduced[5] from the Franck–Condon principle that a change in the distribution of molecules between the vibrational levels of the ground state gives rise to broadening of the absorption band with rise of temperature. In a similar case[6] to that treated here, di(benzothiazol-2-yl) disulphide, such thermal broadening accounts for the whole of the $\Delta\varepsilon$ curve ($\Delta\varepsilon$ being the difference in molecular extinction coefficients between two selected temperatures); a long tail extends into the visible region and is sufficient to give rise, in reasonably strong solutions, to the observed visual thermochromism. Curves of $\Delta\varepsilon$ in the visible and near-ultraviolet region are presented in Fig. 1 for the thermal broadening of band III, and in Fig. 2 for the thermal broadening of band V. The changes in the absolute magnitude of ε for band V are so small that thermochromism could not arise from this cause. $\Delta\varepsilon$ in the region of band IV (530—590 mμ) was never greater than 0·6. The $\Delta\varepsilon$ curves for the fluorinated complex $Cu(TFacac)_2$ are essentially similar, and are not reproduced. The visual thermochromism in relatively concentrated solutions undoubtedly arises from the tail of band III, spreading into the visible through thermal broadening as the temperature increases.

EXPERIMENTAL

Microanalyses and molecular-weight determinations were made by the Microanalytical Laboratory, Imperial College. Infrared spectra were obtained on a Perkin-Elmer model 21 spectrometer with sodium chloride optics and Nujol mulls. Electronic spectra were obtained on a Unicam S.P. 500 spectrometer with reflectance attachments.

Bisacetylacetonatocopper(II).—This had an ebullioscopic molecular weight in benzene of 257·0, and in chlorobenzene of 264·3 (Calc. for $C_{10}H_{14}CuO_4$: *M*, 261·8).

Bistrifluoroacetylacetonatocopper(II).—The complex $Cu(TFacac)_2$, prepared by the recorded method,[2] had m. p. 188° (lit., 189°) and an infrared spectrum in agreement with recorded data.[2] Its ebullioscopic molecular weight in benzene was 369·4, and in chlorobenzene 364·6 (Calc. for $C_{10}H_8CuF_6O_4$: *M*, 369·7). It had $\lambda_{max.}$ 550 and 660 mμ in chlorobenzene.

Bistrifluoroacetylacetonatocopper(II) *Bispyridine Solvate*.—(*a*) The complex $Cu(TFacac)_2$ (0·37 g., 10^{-3} mole), suspended in boiling cyclohexane (50 ml.), was treated dropwise with pyridine (0·24 g., 3×10^{-3} mole). On cooling to 0°, the dark green solution deposited apple-green crystals of the desired *product* which was collected by filtration and washed with a little cyclohexane (Found: C, 45·3; H, 3·5; N, 5·1. $C_{20}H_{18}CuF_6N_2O_4$ requires C, 45·5; H, 3·4; N, 5·3%). It had $\lambda_{max.}$ 636 mμ. (*b*) A saturated solution of the complex $Cu(TFacac)_2$ in boiling pyridine was cooled to 5°; the excess of pyridine was removed from the crystals by pumping at 10°/1 mm. (Found: C, 45·4; H, 3·4; N, 5·2%).

The infrared spectrum of both samples showed bands as follows (cm.$^{-1}$; bands due to pyridine[7] are indicated by P): 1642m (P), 1618s, 1598m, 1573m (P), 1549(sh), 1530s, 1483w (P), 1442w (P), 1300s, 1226m, 1217sh (P), 1193s, 1150w (P), 1129s, 1068m (P), 1059w, 1035m (P), 1006m (P), 948m, 867s, 788s, 756s (P), 735s, and 704s (P).

Bistrifluoroacetylacetonatocopper(II) *Monopyridine Solvate*.—The solvate, $Cu(TFacac)_2$,2-pyridine (0·53 g., 10^{-3} mole) in a weighed flask was kept at 47°/1 mm. until the calculated weight loss for one equivalent of pyridine had occurred. The sage-green crystals of the *product* lost weight extremely slowly under these conditions. No trace of the apple-green colour of the bis-adduct remained, nor was the characteristic colour of the unsolvated complex $Cu(TFacac)_2$ observed under the microscope (Found: N, 3·13. $C_{15}H_{13}CuF_6NO_4$ requires N, 3·1%). The material had $\lambda_{max.}$ 650 mμ. The infrared spectrum showed bands within 2 cm.$^{-1}$ of those observed for the bis-adduct. The absence of the sharp band at 1010 cm.$^{-1}$ characteristic of the parent $Cu(TFacac)_2$, and the marked shifts of bands below 1000 cm.$^{-1}$ relative to the parent compound indicate that the compound is not a 1 : 1 mixture of $Cu(TFacac)_2$,2pyridine and $Cu(TFacac)_2$.

Bistrifluoroacetylacetonatocopper(II) *Bisquinoline Solvate*.—The preparation followed method (*a*) above, and gave pale green crystals of the *complex* (Found: C, 53·4; H, 3·5; N, 4·6. $C_{28}H_{22}CuF_6N_2O_4$ requires C, 53·7; H, 3·5; N, 4·5%). The infrared spectrum showed bands

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[5] Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419.

[6] Brand and Davidson, *J.*, 1956, 15.

[7] Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

(in cm.$^{-1}$) at 1620s, 1563m, 1548w, 1522m, 1501m (Q), 1483w, 1389w, 1360m, 1316m (Q), 1293s, 1226m, 1189s, 1163w, 1140s, 1136(sh), 1040w, 1019w, 959w, 943m, 863m, 817s (Q), 790m, 784m, 762w, 759w, 735s. Bands due to co-ordinated quinoline are marked Q. A monoquinoline compound could not be obtained; when heated to 100°, the crystals decomposed.

Bistrifluoroacetylacetonatocopper(II) *Monoacetone Solvate.*—A 5% solution of the complex $Cu(TFacac)_2$ in acetone was evaporated in a vacuum until royal-blue crystals appeared, then cooled to −80°, whereupon more crystals were obtained; these were collected on a filter previously cooled by solid carbon dioxide, dried very quickly on filter paper, and weighed rapidly. 0·089 g. of the solvate was then kept at room temperature until of constant weight, giving 0·078 g. of the parent $Cu(TFacac)_2$. Thus 0·011 g. of acetone were equivalent to 0·078 g. of $Cu(TFacac)_2$, a molar ratio of 19 : 21, *i.e.*, 1 : 1 within our experimental accuracy. The solvate was stable in the presence of an excess of acetone.

Tetramethylammonium Chloro(*bistrifluoroacetylacetonato*)*ethanolcuprate*(II).—Tetramethylammonium chloride (0·11 g., 10^{-3} mole) and the complex $Cu(TFacac)_2$ (0·37 g., 10^{-3} mole) were dissolved in absolute ethanol (10 ml.). The bright green solution was concentrated by pumping off ethanol until green crystals of the *complex* appeared. These were collected and rapidly sucked dry at the pump (Found: N, 2·61%. $C_{14}H_{20}ClCuF_6NO_4$ requires 2·67%). The salt (0·053 g., 10^{-4} mole), after being shaken with water, gave the parent $Cu(TFacac)_2$ (0·036 g., 10^{-4} mole), and the filtrate, treated with silver nitrate solution, gave silver chloride (Found: Cl, 6·5. Requires Cl, 6·6%). The infrared spectrum showed bands (in cm.$^{-1}$) at 3481 (OH stretch), 1647 (OH def?), 1615s, 1530s, 1485, 1360w, 1292s, 1221m, 1180s, 1132s, 1020m, 949s, 862s, 790m, 781m, 760w, 733s. Attempts to remove the alcohol resulted in decomposition to a mixture of the starting compounds. The analogous bright-green lithium salt was prepared by a similar method, but decomposed in a few minutes at room temperature.

Triphenylmethylphosphonium Iodo(*bistrifluoroacetylacetonato*)*ethanolcuprate*(II) was prepared by a similar method; the dark green crystals decomposed unless kept in an atmosphere of ethanol. The infrared spectrum showed bands due to ethanol, the triphenylmethylphosphonium cation, and the trifluoroacetylacetonate ligand.

A Cambridge-blue salt containing the ethylenediammonium cation was obtained by using ethylenediamine dihydrochloride in ethanol, but this could not be removed from the mother-liquor without substantial decomposition.

Thermochromism Studies.—Spectra were measured in 1-cm. silica cells, on a Unicam S.P. 500 spectrophotometer, with redistilled chlorobenzene as solvent; an electrically heated Adkins block was used to control the temperature of the cells. To avoid errors from the band width of the spectrophotometer, the sensitivity control was used to compensate alterations in the response of the photocells with increasing temperature, the slit width being maintained constant for a given wavelength. A mercury lamp was used to calibrate the wavelength scale at 20° and 75°. The solute concentrations of samples were corrected for the expansion of the solvent at raised temperatures. The absorption curve at 20° was reproducible after 3 cycles of heating and cooling for both complexes $Cu(acac)_2$ and $Cu(TFacac)_2$. Specimen results are given for the complex $Cu(acac)_2$, as 6×10^{-3}M-solution in chlorobenzene, in the Table.

Variation of optical density from 20° to 75° for the complex $Cu(acac)_2$.

λ (mμ)	Slit width (mm.)	Optical density at				
		20°	32°	40°	60°	75°
405	0·064	1·183	1·29	1·378	1·584	—
420	0·057	0·627	0·729	0·762	0·873	0·915
430	0·052	0·386	0·45	0·482	0·585	0·609
440	0·050	0·229	0·27	0·292	0·351	0·396
450	0·047	0·140	—	—	—	—
460	0·045	0·098	0·111	0·123	0·147	0·171
470	0·043	0·085	—	0·101	—	0·125
480	0·040	0·094	0·101	0·103	0·112	0·119
490	0·039	0·110	—	0·118	—	0·130
500	0·038	0·135	—	0·141	0·141	0·140

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