1031. *Some Quinqueco-ordinated Copper*(II) *Complexes.*

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The adduct of quinoline with bisacetylacetonatocopper(II) has been re-examined and it is confirmed that it contains quinqueco-ordinated copper(II), as do the monohydrate of *NN'*-bis(acetylacetonato)ethylenedi-iminocopper(II), and the adduct of this complex with ethylenediamine hydrate.

Bisacetylacetonatocopper(II) in moist dichloromethane, when treated with picric acid, forms diaquoacetylacetonatocopper(II) picrate, which contains copper atoms surrounded by five oxygen atoms in a square pyramid.

Potassium pentanitrocuprate(II) is shown to contain discrete anions with the copper atom in each co-ordinated through nitrogen to five nitrite groups.

Bis(*acetylacetonato*)*quinolinecopper*(II).—The introduction of additional ligands along the axis normal to the molecular plane of planar complexes has recently aroused much interest. Spectral evidence [1] is available for the co-ordination of heterocyclic bases to bisacetylacetonatocopper(II), and a 1 : 1 adduct of this complex with 4-methylpyridine has been isolated; [2] the base is lost very readily. Although numerous cases of quinqueco-ordinated copper are now known, it appears to have been overlooked that, many years ago, Morgan and Moss [3] noticed the formation of an adduct between bisacetylacetonato-copper(II) and quinoline, which was later obtained pure, shown [4] to be a 1 : 1 adduct, and formulated as containing quinqueco-ordinated copper(II). The statement was made [4] that " one of the characteristic co-ordination numbers of copper is five."

We find that the sage-green adduct loses quinoline rather readily in air, but may be kept indefinitely in a sealed tube and is stable in an atmosphere containing quinoline vapour. The stoicheiometry is 1 : 1. *X*-Ray powder photographs show that the unit cells of the adduct and parent compound are very different. Details of the infrared spectra are shown in Table 1.

The adduct shows several bands due to quinoline, but the similarity of the spectra in the region 1530—1590 cm.$^{-1}$ suggests that no great change has occurred in the environment of the oxygen atoms; we have confirmed this by measuring the extinction coefficients (see Table 2) of the two strong bands in both compounds, using dichloromethane as solvent.

The visible absorption spectrum of bisacetylacetonatocopper(II) in dichloromethane ($\lambda_{1\text{max.}}$ 658 mμ, ε 41; $\lambda_{2\text{max.}}$ 550, ε 34) changes when quinoline is added, the successive absorption curves showing a sharp isosbestic point at 570 mμ, indicating a two-phase

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[1] Graddon, *Nature*, 1959, **183**, 1610; Graddon and Watton, *J. Inorg. Nuclear Chem.*, 1961, **21**, 49.
[2] Walker, *Austral. J. Chem.*, 1961, **14**, 161.
[3] Morgan and Moss, *J.*, 1914, **105**, 189.
[4] Morgan and Smith, *J.*, 1926, 912.

TABLE 1.

Infrared spectra (for mulls) of bisacetylacetonatocopper(II) (A) and its adduct (B) with quinoline.

A		2918w			1582s ‡	1557w *	1533s ‡		1416m	1357m
B	2950sh	2920m	1627w	1614w	1587s	1556w *	1532s	1508m †	1411m	1355m
A		1277m	1190s	1020m	938s			787s	782s	685w
B	1320m	1272m	1190s	1018m	945m	933m	805s		783m	670w

* These weak peaks are probably due to a crystal effect; similar small peaks are observed in other solid acetylacetonates. † This probably arises from co-ordinated quinoline; we find that dichlorobisquinolineplatinum(II) has a peak at 1510 cm.$^{-1}$. ‡ For chloroform solution, these absorptions occur at 1577 and 1525 cm.$^{-1}$.

TABLE 2.

Extinction coefficients of carbonyl and olefinic stretching absorptions.

	ν_1 *	ε_1 †	ν_2	ε_2
Bisacetylacetonatocopper(II)	1579	760	1526	1080
Quinoline adduct	1578	800	1525	1120

* Frequencies in cm.$^{-1}$. † ε is the extinction coefficient per g.-atom of copper.

equilibrium. The peak at 550 mμ disappears, and that at 658 mμ shifts to 650 mμ (ε 71). These results agree with the measured spectrum of bisacetylacetonatocopper(II) in pure quinoline as solvent ($\lambda_{max.}$ 650 mμ, ε 70). The spectrum in quinoline, as might be expected, is very similar to that in pyridine.[5] The calculated equilibrium constant (at 30°) is of the form

$$K = [Cu(acac)_2Q]/[Cu(acac)_2][Q] = 1{\cdot}5 \pm 0{\cdot}1$$

Some other potential fifth ligands have been examined preparatively, with no success. For example, when bisacetylacetonatocopper(II) in chloroform is refluxed with excess of triphenylphosphine a green solution is produced; however, the solid obtained on removal of the solvent is always a mixture of the two components, with no indication of an adduct.

The NN′-*Bis*(*acetylacetonato*)*ethylenedi-iminocopper*(II) *System.—The hydrate.* *NN′*-Bis(acetylacetonato)ethylenedi-iminocopper(II), hereafter called Cuec, was obtained by Morgan and Smith [4] as purple crystals, which formed a green monohydrate. We find that the water molecule is very weakly held, and that when the hydrate was crushed or powdered to prepare a mull, its colour changed from green to purple. We have therefore measured the infrared spectrum of a single crystal; this is compared with the spectrum of the parent compound in Table 3. The bands which appear in the spectrum of the hydrate but not in the anhydrous compound are presumably due to vibrations of the water molecule. The remainder of the spectrum is almost unchanged, suggesting that the environment of the ligand does not alter greatly.

TABLE 3.

Infrared absorption bands (cm.$^{-1}$) of the anhydrous and hydrated compounds.

Cuec *	—	—	2916w	2868sh	—	1598s	1525s	1417s	1350m	1280m	1263sh
Cuec, H_2O †	3560	3480	2910w	2855sh	1660s	1600m	‡	‡	1350m	1299w	1261sh
Cuec *	—	1222m	—	1114m	1070w	1039m	1020w	—	942m	753s	736m
Cuec, H_2O †	1235w	1218m	1201m	1115s	—	1030s	1018s	972m	942s	755s	744s

* In mulls. † As single crystal. ‡ A very broad absorption occurs between 1400 and 1550 cm. ^{1}, which did not show distinct peaks.

The change in colour which occurred when the hydrate was powdered was further examined by means of the visible transmission spectra of the solids and by *X*-ray powder photographs. A flat sheet of the hydrate had bands at 564 (weaker) and 634 mμ (stronger),

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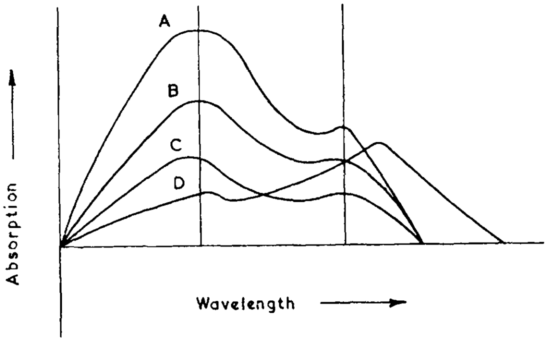
[5] Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.

while the purple material formed by crushing the hydrate had bands at 560 (stronger) and 630 mμ (weaker), closely resembling the authentic anhydrous material, either as a mull or as thin crystals. These spectra are shown in the Figure. The increase in the relative intensity of the band at higher wavelengths is noteworthy, since this occurs in other cases where the co-ordination number of copper increases. From *X*-ray powder photographs, it appears that the purple form produced by crushing is that particular polymorph (there are at least three) obtained by crystallization from benzene, which we call form B.

The green hydrated flakes develop purple patches, which, unlike the green substrate, exhibit a pronounced dichroism, indicative of an epitaxially ordered growth. The purple encrustation may readily be removed by washing with cyclohexane, and a comparison of Weissenberg photographs before and after washing shows that the purple encrustation must be form B (see Experimental section for coding); the structure of form B has been published,[6a] and we have stopped our work on this problem since we have been informed [6b] that the structure of the hydrate is being investigated.

It is interesting that the green monohydrate of bis(salicylaldehydato)propylenedi-iminocopper(II), shown [7] to contain quinqueco-ordinated copper by *X*-ray examination, does not change colour on powdering; the infrared spectrum shows bands characteristic of water. Studies of " solvates " of copper compounds which involve powdering or pressing into potassium bromide discs are obviously dangerous, so that results [8] based on spectral studies of samples prepared in these ways are not conclusive.



Spectra of (A) Cuec as mull, (B) Cuec as thin crystals, (C) the purple product of crushing Cuec,H_2O, and (D) Cuec,H_2O as thin sheet.

The adduct with ethylenediamine hydrate. Morgan and Smith [4] found that when *NN'*-bis(acetylacetonato)ethylenedi-iminocopper(II) was crystallized from ethylenediamine hydrate, the product was the 1 : 1 adduct with ethylenediamine hydrate. We have prepared this compound as green plates and find that it is very similar to the hydrate in that the addend is lost very readily, for example, on powdering. The visible spectrum, obtained by reflectance, was rather similar to that of the hydrate, with peaks at 560 (weaker) and 650 mμ (stronger). The infrared spectrum of the crystal showed strong bands in the region 3300—3400 cm.$^{-1}$ which did not appear in that of the parent compound. When kept over calcium chloride, the adduct lost ethylenediamine hydrate, but we found no evidence for the dimeric ethylenediamine-bridged compound ecCuenCuec which Morgan and Smith claimed to have made. The loss of ethylenediamine hydrate occurs with direct formation of the parent compound. When crushed, the compound became purple and had peaks at 540 (stronger) and 638 mμ (weaker), comparable with the authentic anhydrous Cuec.

Diaquoacetylacetonatocopper(II) *Picrate.*—When molar amounts of bisacetylacetonatocopper(II) and picric acid are mixed in dichloromethane, a green solution is formed which,

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[6] (*a*) Hall, Rae, and Waters, *Proc. Chem. Soc.*, 1962, 143; (*b*) Hall and Waters, personal communication.

[7] Llewellyn and Waters, *J.*, 1960, 2639.

[8] Waters and Hall, *J.*, 1959, 1203.

when kept at room temperature, very slowly deposits beautiful dark green needles of diaquoacetylacetonatocopper(II) picrate. If the solvent used is saturated with water before the reaction, the green crystals appear more rapidly; they are not formed at all under strictly anhydrous conditions. In our initial preparation, the water molecules were absorbed from the air. The stoicheiometry of the reaction is:

$$Cu(C_5H_7O_2)_2 + C_6H_2(NO_2)_3(OH) + 2H_2O \rightleftharpoons [Cu(C_5H_7O_2)(H_2O)_2][C_6H_2(NO_2)_3O] + C_5H_8O_2$$

Acetylacetone may be recognized in the mother-liquor from the preparation. A more convenient preparation involves fusing moist picric acid and an excess of bisacetylacetonatocopper(II), cooling, and extracting the reaction mixture with boiling water; on cooling of the dark green aqueous solution, the salt crystallizes. Several violent explosions occurred when this second method was used, and it is recommended only for extremely small-scale work.

The preparation in dichloromethane is often complicated by the formation of non-stoicheiometric adsorption complexes of bisacetylacetonatocopper(II) and picric acid; these may be recognized by their colour (yellow-green), their microcrystalline character, and, above all, their fission by water, which dissolves the picric acid as such and leaves blue bisacetylacetonatocopper(II) undissolved. Diaquoacetylacetonatocopper(II) picrate, on the other hand, dissolves unchanged in water to give a greenish-yellow solution.

The compound diaquoacetylacetonatocopper(II) picrate is magnetically dilute, with $\mu_{eff} = 1{\cdot}98$ B.M. at room temperature; analytical results, combined with the molecular weight determined by the *X*-ray method, lead to the formulation given, which is supported by the conductivity in aqueous solution, characteristic of a 1 : 1 electrolyte, and the infra-red spectrum which shows bands due to picrate, water, and co-ordinated acetylacetone.

The three-dimensional *X*-ray study of the compound[9] is sufficiently advanced for the following points to be made. The copper atoms are all in identical environments, with four oxygen atoms approximately in a plane around each copper (two from the acetylacetone at 1·88 Å, and two from the water at 1·95 Å). A fifth oxygen (the phenol-oxygen of the picrate residue) is at the apex of a square pyramid, the Cu–O distance here being 2·76 Å. The sixth apex of the octahedron about the copper is occupied by the γ-carbon of an acetylacetone residue in another layer; the Cu–C distance is about 3·1 Å. Recently, several complexes of platinum have been shown[10] to contain bonds between this γ-carbon and the metal; the Pt–C distances are 2·39—2·56 Å, so we prefer to regard the Cu–C distance of 3·1 Å as a non-bonding distance.

Several picric acid " adducts " of complexes of copper(II) with tetradentate Schiff bases have been reported, particularly by Tanaka.[11] In view of the surprising structure of the " adduct " we described here, much of the work on complexes of Schiff bases needs re-examination.

The Pentanitrocuprate(II) *Anion.*—Nitrite ion combines with copper(II) to form several species, which have been studied in aqueous solution[12] by spectrophotometry, and in the solid state[13] by *X*-ray methods, which gave unit cells and space groups for several compounds, among them potassium pentanitrocuprate(II), first adequately described by Kurtenacker.[14] We have confirmed the crystallographic results obtained by Ferrari, Nardelli, and Bigliardi,[13] and have further characterized the compound, as a preliminary to a full *X*-ray examination.

The infrared spectrum of potassium pentanitrocuprate(II), in the sodium chloride region, shows that no water is present. It also shows frequencies at 1351 (ν_3, NO asymm.

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[9] Rogers, personal communication.

[10] Swallow and Truter, *Proc. Roy. Soc.*, 1960, *A*, **254**, 205; Hazell and Truter, *ibid.*, p. 218.

[11] Tanaka, *J. Amer. Chem. Soc.*, 1958, **80**, 4108.

[12] Kossiakoff and Sickman, *J. Amer. Chem. Soc.*, 1946, **68**, 442.

[13] Ferrari, Nardelli, and Bigliardi, *Gazzetta*, 1958, **88**, 827.

[14] Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204.

str.), 1188 (ν_1, NO symm. str.), and 816 cm.$^{-1}$ (ν_2, NO_2 bend). An overtone of the ν_3 band appears weakly at 2708 cm.$^{-1}$. There are also weak shoulders at 1340, 1212, and 822 cm.$^{-1}$, suggesting that two types of NO_2 group are present, both possessing C_{2v} symmetry (*i.e.*, co-ordinated through nitrogen or not at all). However, it also known[15] that, as the number of identical nitrite groups co-ordinated to a metal atom increases, the three fundamental vibrations of the nitro-group often split. The most important conclusion from the spectrum in the sodium chloride region is that no significant deviation from C_{2v} symmetry occurs; there appear to be no M–ONO bonds or bridging nitrite groups, as the bands characteristic[16] of these species do not appear. The spectrum in the potassium bromide region supports this conclusion, as only one strong band (at 417 cm.$^{-1}$) appears in the region where metal–ligand vibrations are expected to occur, although three very weak bands appear at 471, 457, and 441 cm.$^{-1}$ which may be due to M–NO_2 wagging.

We have found that potassium pentanitrocuprate(II), though insoluble in ethanol, may be recrystallized rapidly from methanol, whereas aqueous solutions, even when ice-cold, slowly deposit a turquoise-blue solid, probably having the structure $K[Cu(NO_2)_3H_2O],H_2O$; its infrared spectrum shows bands due to (*a*) nitrite groups co-ordinated through nitrogen, at 1328 (ν_2), 1238 (ν_3), and 820 (ν_1), (*b*) co-ordinated water, at 3490 (stretch), 1630 (def), and 1012 and 923 (wag and rock), and (*c*) hydrogen-bonded water, at 3150 (stretch) and 1950 cm.$^{-1}$ (def; v. broad). Two further weak broad bands appear at 850 and 737 cm.$^{-1}$. It has been pointed out[17] that co-ordinated water does not give rise to the wagging and rocking modes around 1000 cm.$^{-1}$ unless it is fairly strongly hydrogen-bonded.

We have measured the variation with temperature of the magnetic susceptibility of potassium pentanitrocuprate(II). Our findings are shown in Table 4. The Curie–Weiss law is obeyed, with a θ value of *ca.* 5°, so that the copper atoms are certainly magnetically dilute. In view of the small effect of comparatively large stereochemical changes on the magnetic behaviour of copper(II), we have not attempted to produce a calculated curve.

TABLE 4.

Variation of the magnetic susceptibility of the salt $K_3[Cu(NO_2)_5]$ with temperature.

Temp. (K)	280·7°	257·2°	226·5°	208·3°	172·0°	136·8°	116·4°
$10^6\chi_m$ (corr.) (c.g.s.u.)	1762	1900	2265	2500	3030	4010	5180
μ_{eff}	2·00	1·99	2·03	2·05	2·05	2·10	2·20

Diamagnetic correction taken as -140×10^{-6} c.g.s.u.

EXPERIMENTAL

Microanalyses were made and molecular weights determined by the Microanalytical Laboratory, Imperial College.

Infrared spectra were recorded by using a Perkin-Elmer model 21 spectrometer with sodium chloride and calcium fluoride optics, and a Grubb-Parsons grating instrument in the far-infrared, for Nujol, Fluorolube, or hexachlorobutadiene mulls. Electronic spectra were taken on a Perkin-Elmer model 4000 spectrometer; reflectance spectra were obtained by using the reflectance attachment to a Unicam S.P. 500 spectrophotometer. Magnetic measurements were made by the standard Gouy procedure. *X*-Ray powder photographs were taken in Lindemann tubes with a 9-cm. Unicam camera on a Raymax *X*-ray set with a copper target and a nickel filter.

Bis(*acetylacetonato*)*quinolinecopper*(II).—The procedure of Morgan and Smith,[4] which gives brown oxidation products of quinoline, was modified as follows: Bisacetylacetonatocopper(II) (2·61 g., 0·01 mole) was dissolved in quinoline (10 ml.) and heated to 240° under nitrogen. After 2 min., the mixture was filtered, and the saturated solution thus obtained was allowed to cool slowly in an atmosphere of nitrogen. The adduct (2·7 g., 70%) separated as

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[15] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

[16] Nakamoto, Fujita, and Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

[17] Fujita, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.

sage-green needles, which were collected, sucked as dry as possible, and washed with cyclohexane (Found: C, 58·1; H, 5·5; N, 3·9. Calc. for $C_{19}H_{21}CuNO_4$: C, 58·4; H, 5·4; N, 3·6%). The magnetic moment of the copper atom is 1·98 ± 0·05 B.M. at 25°. The large uncertainty is due to the very great difficulty in packing the tube.

Bisacetylacetone Ethylenedi-imide.—This was prepared by Combes's method;[18] after three recrystallizations from water, the white crystals had m. p. 110° (lit., 111°) (Found: C, 64·2; H, 8·8. Calc. for $C_{12}H_{20}N_2O_2$: C, 64·25; H, 9·0%). The dihydrochloride was also made by Combes's method and had m. p. 278° (decomp.) (lit., 280°).

(*Bisacetylacetonato*)*ethylenedi-iminocopper*(II).—This was obtained as purple needles from benzene, as described by Morgan and Smith.[4] It had m. p. 140 (lit., 137°) [Found: C, 50·3; H, 6·2; N, 9·6%; *M*, 312 (ebullioscopic in benzene). Calc. for $C_{12}H_{18}CuN_2O_2$: C, 50·4; H, 6·35; N, 9·8%; *M*, 286].

Polymorphs of this compound are known; details are given in Table 5. In form A (Found: C, 50·4; H, 6·2. Calc. for unsolvated Cuec, $C_{12}H_{18}CuN_2O_2$: C, 50·4; H, 6·35%) no ethoxy-groups were present (Zeisel's method), and no bands due to ethanol appeared in the infrared spectrum. Nor did the infrared spectrum show bands characteristic of ethanol which has added across a double bond; such bands have been found[19] for certain " ethanolates " of other copper(II) compounds with Schiff bases. In form B, from benzene, no benzene could be detected on heating the crystals, not even on melting them. Crystals obtained from other simple organic solvents, such as acetone or methanol, did not contain molecules of solvent.

TABLE 5.

Properties of polymorphs of *NN'*-bis(acetylacetonato)ethylenedi-iminocopper(II).

	Ref. 6*b*		This work		Ref. 6*b*
Prepn.	*	—	From EtOH	From C_6H_6	—
M. p.	—	—	140	140	—
Space group	?	*Pbcn*	*Pbcn*	$P2_1/_c$	$P2_1/_c$
a Å	17·30	17·03	16·87	10·85	11·02
b Å	7·78	7·96	8·12	8·94	8·97
c Å	20·26	19·60	19·45	13·05	13·10
β	106°	—	—	95°	94°
Volume (Å^3)	2620	2658	2664	1260	1287
Z	8	8	8	4	4
d_0 (g. cm.$^{-3}$)	—	—	1·44	—	—
d_c (g. cm.$^{-3}$)	1·45	$1{\cdot}43_0$	$1{\cdot}42_5$	1·51	$1{\cdot}47_5$
Form	—	A	A	B	B

* This third form may be the same as a polymorph (m. p. 140°) that we have obtained, but not investigated, from cyclohexane.

On exposure of the B form to moist air, the green monohydrate was slowly formed.

NN'-*Bis*(*acetylacetonato*)*ethylenedi-iminocopper*(II) *Monohydrate.*—When a solution of the anhydrous compound in 1 : 1 v/v acetone–water was allowed to crystallize slowly, green mica-like plates of the desired compound were obtained (Found: C, 47·8; H, 6·8. Calc. for $C_{12}H_{20}CuN_2O_3$: C, 47·4; H, 6·6%). The compound lost water in dry air, particularly from imperfections in the crystal. Any purple anhydrous material which was formed on the green plates could be washed away with cyclohexane, which is the only organic solvent found not to cause decomposition of the hydrate. When the hydrate was heated, the loss of water became more and more rapid, until at 60°, a green crystal became perceptibly purple in 5 sec. The purple anhydrous B form produced melts at 140° (lit., 137°). In a preliminary *X*-ray investigation of our badly twinned crystals, the following information was obtained: $a = 11{\cdot}8$, $b = 5{\cdot}6$, $c = 20{\cdot}5$ Å, $\beta = 101°$, $Z = 4$. These values agree well with data[6b] from New Zealand for the hydrate.

NN'-*Bis*(*acetylacetonato*)*ethylenedi-iminocopper*(II) *Ethylenediamine Solvate Hydrate.*—When a hot solution of the parent compound in ethylenediamine hydrate was allowed to cool slowly, grass-green plates of the adduct were obtained (Found: C, 45·8; H, 7·4; N, 15·25. Calc. for

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[18] Combes, *Compt. rend.*, 1889, **108**, 1252.

[19] Harris and McKenzie, *Nature*, 1962, **196**, 670.

$C_{14}H_{28}CuN_4O_3$: C, 46·2; H, 7·75; N, 15·4%). The infrared spectrum of the crystals, viewed perpendicular to the flat faces, showed absorptions (in cm.$^{-1}$) at 3600—3050 (v. broad, centred at ~3200) (OH and NH stretching), 2910 (CH stretch), 1660 (weak) (OH def?), 1582 (strong) (NH def.), 1497, 1476, 1409, 1324, 1236, 1214, 1113, 1050, 1012, 981, 824 (broad), and 746 (broad). The compound lost ethylenediamine hydrate in dry air or when kept over fused calcium chloride. This process was followed by weighing small samples twice a day for 2 weeks, there being no sign of constant weight until the parent compound was left. The curve of loss of weight against time was exponential for 10 days; after 6 days, analysis of the green material gave C, 46·3; H, 7·7; N, 15·95%, whereas the dimer, $C_{26}H_{44}N_6O_4Cu_2$, requires C, 49·4; H, 7·0; N, 13·3%. The loss of addend occurred most readily at defects in the crystal. When heated, the anhydrous B form parent compound was formed rapidly at 70°, and this melted at 140°.

The infrared spectra of the flat crystals of the hydrate and ethylenediamine solvate hydrate were obtained perpendicular to the flat surfaces by mounting the crystal between two sodium chloride plates and running this against two similar sodium chloride plates as a blank. For visible spectra, the monohydrate was mounted as a flat, single crystal between two microscope slides, and run against Nujol-soaked filter paper similarly mounted as a blank. The spectrum of the ethylenediamine hydrate adduct was obtained by using the reflectance attachment.

NN′-*Bis*(*salicylaldehydato*)*propylenedi-iminocopper*(II) *Hydrate*.—The ligand (2·8 g., 0·01 mole) in alcohol (20 ml.) was slowly added to a solution of copper acetate (2·0 g., 0·01 mole) in water (10 ml.) which had been treated with ammonia till the precipitated copper hydroxide just redissolved. The crude purple precipitate of bis(salicylaldehydato)propylenedi-iminocopper(II) was collected, washed with water, air-dried, and recrystallized from benzene (Found: C, 59·1; H, 4·55; N, 7·9. Calc. for $C_{17}H_{16}CuN_2O_2$: C, 59·35; H, 4·7; N, 8·15%). Infrared absorption occurred at 2670w, 1938w, 1643s, 1603s, 1547s, 1393m, 1342m, 1319m, 1250m, 1200s, 1154s, 1132m, 1118m, 1051m (this band does not appear in the hydrate), 1031m, 970m, 924m, 906s, 850m, 798m, 754s, and 738s cm.$^{-1}$. When a saturated solution of this compound in 10 : 1 v/v acetone–water was allowed to crystallize, the product was the desired green monohydrate (Found: C, 56·7; H, 5·2; N, 7·7. Calc. for $C_{17}H_{18}CuN_2O_3$: C, 56·1; H, 5·0; N, 7·7%). The infrared spectrum showed absorptions at 3400(bd),* 3200(bd),* 2660w, 1940w, 1781w,* 1644s, 1601s, 1532s(bd), 1397(sh),* 1392m, 1342m, 1310s(bd), 1236m, 1193s, 1155s, 1133s, 1121w,* 1116w, 1094m,* 1038m, 1014s,* 987s,* 979w,* 972m, 941w,* 936w,* 924m, 906s, 858s, 794s, 764s,* 760s, 746, 744s, and 711m* cm.$^{-1}$. Bands marked with an asterisk do not appear in the anhydrous material.

Diaquoacetylacetonatocopper(II) *Picrate*.—Bisacetylacetonatocopper(II) (0·26 g., 1 mmole) and picric acid (0·23 g., 1 mmole) were dissolved in dichloromethane (30 ml.) previously saturated with water. After 14 days, the dark-green crystals of the desired *product*, which had separated, were collected (0·49 g., 90%) [Found: C, 31·1; H, 3·2; Cu, 14·8; N, 10·0%; *M* (*X*-ray method), 430 ± 5. $C_{11}H_{13}CuN_3O_{11}$ requires C, 31·0; H, 3·1; Cu, 14·9; N, 9·85%; *M*, 426·8]. $\mu_{\rm eff}$ (Gouy) was 1·98 B.M.

The compound recrystallized unchanged from 95% alcohol or water; it is slightly soluble in dichloromethane and chloroform.

Infrared bands (in cm.$^{-1}$), with assignments where these are reasonable, were at: 3360m (OH str.), 3065w (νC_{Ar-H}), 2936w, 2854w, 2730w, 1793w, 1643m (OH def.), 1620(sh), 1573s (νCO in acac), 1542w (νNO asymm.), 1521m (νC=C in acac), 1504w (Ring A_1 νC–C) 1447vw, 1418w (Ring B_1 νC–C), 1378m, 1354(sh) (νNO symm.), 1337m (νNO symm?), 1309m, 1272m (Ring B_1 νC–C), 1156m (βCH), 1141(sh), 1074m (νCH), 1016m, 987w (co-ord. H_2Owag?), 970w, 939w (γ)CH, 926w, 913w (νCN), 822m (νCN), 789m, and 737m (γCH). Many of the "picryl" bands which appear here agree closely with the measurements of Dyall.[20]

Acetylacetone was recovered from the mother-liquor of the preparation by vacuum-distillation. The distillate was dried with calcium chloride and shown to contain acetylacetone by the identity of its infrared spectrum with that of authentic material, by conversion, through the addition of ferric chloride and sodium hydrogen carbonate solution, into the blood-red ferric acetylacetonate, and finally by shaking with ammoniacal copper sulphate solution which gives bisacetylacetonatecopper(II).

Potassium Pentanitrocuprate(II).—The preparation followed ref. 13, except for the obvious misprint in that paper, where 30 : 1 should read 3 : 1. The product was recrystallized rapidly

[20] Dyall, *Austral. J. Chem.*, 1961, **14**, 493.

from methanol, potassium pentanitrocuprate(II) being obtained as long dark green needles (Found: Cu, 15·4; N, 17·3. Calc. for $CuK_3N_5O_{10}$: Cu, 15·4; N, 17·0%). The reflectance spectrum of the powdered compound in the visible region showed a broad absorption with a maximum at 680 mμ. When the pentanitro-salt was dissolved in cold water, a turquoise-blue powder was rapidly formed, which was collected, washed with water, and dried over calcium chloride. It is considered to be *potassium aquotrinitrocuprate*(II) *monohydrate* (Found: Cu, 23·4; N, 15·0. $CuKH_4N_3O_8$ requires Cu, 23·0; N, 15·2%).

We thank Mr. M. Gerloch and Mr. G. C. Nicholson, respectively, for assistance with magnetic and *X*-ray measurements, Peter Spence Ltd. for a gift of bisacetylacetonatocopper(II), and the Hercules Powder Co. for financial support.

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[*Received, March* 28*th*, 1963.]