Structural Studies of Metal Complexes with ω-Nitroacetophenone. Crystal Structures of Bis-(ω-nitroacetophenonato)copper(II), and of its Addition Complexes with 2- and 4-Methylpyridine (α- and γ-Picoline)

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The crystal and molecular structure of bis-(ω-nitroacetophenonato)copper(II) (1) and of its addition complexes, (2) and (3), with α- and γ-picoline (2- and 4-methylpyridine respectively) have been determined and refined by anisotropic least-squares methods to final *R* values of 0·072, 0·096, and 0·072. Crystal data: (1), triclinic, space group $P\bar{1}$, $a = 5{\cdot}453 \pm 0{\cdot}01$, $b = 8{\cdot}183 \pm 0{\cdot}01$, $c = 9{\cdot}506 \pm 0{\cdot}01$ Å, $\alpha = 109° 55' \pm 10'$, $\beta = 104° 52' \pm 10'$, $\gamma = 90° 21' \pm 10'$, $Z = 1$; (2), triclinic, space group $P\bar{1}$, $a = 10{\cdot}537 \pm 0{\cdot}01$, $b = 8{\cdot}624 \pm 0{\cdot}01$, $c = 12{\cdot}089 \pm 0{\cdot}01$ Å, $\alpha = 93° 18' \pm 10'$, $\beta = 94° 20' \pm 10'$, $\gamma = 92° 21' \pm 10'$, $Z = 2$; (3), monoclinic, space group $C2/c$, $a = 19{\cdot}238 \pm 0{\cdot}010$, $b = 9{\cdot}268 \pm 0{\cdot}005$, $c = 17{\cdot}710 \pm 0{\cdot}010$ Å, $\beta = 120° 5' \pm 5'$, $Z = 4$. The environment of the copper atom is pseudo-octahedral for (1). The copper atom co-ordination is tetragonal pyramidal for (2) and pseudo-octahedral for (3). The N-bases are co-ordinated on the basal plane of the pyramid in (2) and on the equatorial plane in (3). This causes displacement in the axial position of one of the oxygen atoms for one ligand molecule in (2) and for both the ligand molecules in (3).

THE ability of organic nitro-groups to form chelate complexes in which the $-NO_2$ group participates directly in the chelation has been studied.[1] The complexes of formulae $M(\omega\text{-nap})_2$ were prepared from ω-nitroacetophenone $PhCO{\cdot}CH_2{\cdot}NO_2$ (ω-nap) and bivalent first-transition series metals; the stereochemistry and electronic structure of these complexes have been investigated by spectrophotometric, magnetic, crystallographic, and molecular weight measurements.[2,3] Only the copper and manganese complexes are stable in air, but the copper complex gives single crystals suitable for *X*-ray analysis. The structure analysis of this complex is useful in establishing the co-ordinating properties of a molecule such as ω-nitroacetophenone compared with β-diketones as complexing agents. Owing to the weak ligand field of the α-nitro-ketonic group, the chromophore, MO_4, present in $M(\omega\text{-nap})_2$ complexes has a marked tendency to co-ordinate in the fifth and sixth co-ordination positions. The interaction between $Cu(\omega\text{-nap})_2$ (1) and heterocyclic N-bases shows the formation of mono- and bis-adducts. Magnetic and spectral

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[1] C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **40**, 558.

[2] C. Ercolani, I. Collamati, and D. J. Machin, *J. Chem. Soc.* (*A*), **1969**, **1537**.

[3] I. Collamati and C. Ercolani, *J. Chem. Soc.* (*A*), 1969, 1541.

data of these complexes support a six-co-ordinate octahedral structure.[4]

An exception is the mono-addition complex (2) with 2-methylpyridine (α-pic) which is a five-co-ordinate complex. The absorption spectrum of this compound is quite different from that of the six-co-ordinate species of this class.[5] It is, therefore, necessary to make a structural investigation to determine the ligand arrangement around the metal ion.

The bis-adducts were isolated in at least two different forms: a yellow form (centrosymmetric from unit-cell data) found to be pseudo-octahedral from spectral and magnetic properties with axial co-ordination of the N-base molecules, and a green form for which the ligand arrangement is uncertain. The bis-(4-methylpyridine) (γ-pic) adduct (3) appears to behave spectrochemically like the green form and to be stable to *X*-rays. In order to determine the ligand arrangement around the copper atom for this class of complexes, a single crystal *X*-ray analysis was undertaken on the bis-γ-pic adduct.

Preliminary notes on the crystal structure analysis of Cu(ω-nap)$_2$ and of [Cu(ω-nap)$_2$(α-pic)] have been reported previously.[6,7]

TABLE 1

Co-ordinates (× 10^4) and temperature factors,* with standard deviations in parentheses, for Cu(ω-nap)$_2$, (1)

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cu	0	0	0	219(4)	19(4)	88(3)	165(2)	26(3)	66(1)
O(1)	714(7)	1172(6)	2219(4)	247(14)	12(17)	97(13)	191(9)	35(10)	84(5)
O(2)	−2703(8)	−1536(6)	−2(4)	323(16)	17(17)	130(14)	164(8)	34(10)	82(5)
O(3)	−6275(8)	−1849(6)	564(5)	298(16)	143(19)	78(16)	180(9)	56(12)	132(6)
N	−4074(9)	−1071(6)	992(5)	257(17)	10(18)	92(15)	133(9)	69(12)	94(6)
C(1)	−3245(10)	175(8)	2422(8)	259(20)	31(22)	106(18)	164(11)	54(14)	87(7)
C(2)	−832(10)	1154(7)	3017(6)	265(19)	100(19)	110(17)	122(9)	59(12)	79(6)
C(3)	−42(10)	2272(7)	4686(6)	246(19)	110(20)	96(17)	139(10)	56(13)	79(6)
C(4)	2142(12)	3464(9)	5242(7)	329(23)	2(24)	125(20)	165(12)	48(15)	96(8)
C(5)	2959(13)	4521(10)	6797(7)	411(27)	54(29)	52(23)	175(13)	19(16)	103(8)
C(6)	1598(14)	4422(9)	7827(7)	492(31)	91(29)	85(24)	160(13)	26(16)	90(8)
C(7)	−577(15)	3237(10)	7291(8)	555(34)	143(34)	275(28)	215(15)	103(19)	103(9)
C(8)	−1400(12)	2181(9)	5738(7)	348(24)	92(25)	155(20)	177(13)	69(15)	85(7)
				$B/\text{Å}^2$					
H(1)	−4422	420	3105	4·00					
H(4)	3121	3554	4509	4·00					
H(5)	4533	5358	7183	4·00					
H(6)	2179	5198	8946	4·00					
H(7)	−1543	3151	8030	4·00					
H(8)	−2974	1346	5358	4·00					

* For non-hydrogen atoms, exponential coefficients b_{ij} as given here are defined by

$$T = \exp[10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

EXPERIMENTAL

Preparations.—The complexes were prepared according to the methods of refs. 2—4. Crystals of (1) were obtained by recrystallization from acetone as red-brown prisms, stable in air and to *X*-rays. (2) and (3) were obtained as prisms from acetone containing a small amount of the appropriate base. Crystals of (3) are stable in air and to *X*-rays, those of (2) are strongly pleochroic (green and brown), stable in air, and rather unstable to *X*-rays; thus a number of crystals had to be used for data collection.

Crystal Data, Intensity Measurements, and Corrections.—The unit-cell dimensions were determined by a modified, improved, version of Christ's method [8] from zero-layer Weissenberg films taken about the *a* and *b* axes for Cu(ω-nap)$_2$ and for [Cu(ω-nap)$_2$(α-pic)], and about the *b* and *c* axes for [Cu(ω-nap)$_2$(γ-pic)$_2$], using mainly reflections from Cu-$K_{\alpha1}$ radiation ($\lambda = 1{\cdot}54056$ Å). Intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs. Intensity data were corrected for Lorentz and polarization effects, and for spot extension.[9] First scaling of observed structure amplitudes was performed by use of the least-squares procedure of Rollett and Sparks.[10] Final scaling with an independent scale-factor for each unmerged layer was done at the end of isotropic least-squares refinement, after the introduction of hydrogen atoms into the structure-factor calculation.

Bis-(ω-nitroacetophenonato)copper(II). [Cu(ω-nap)$_2$], (1), $C_{16}H_{12}CuN_2O_6$, $M = 391{\cdot}828$, Triclinic, $a = 5{\cdot}453 \pm 0{\cdot}01$, $b = 8{\cdot}183 \pm 0{\cdot}01$, $c = 9{\cdot}506 \pm 0{\cdot}01$ Å, $\alpha = 109° 55' \pm 10'$, $\beta = 104° 52' \pm 10'$, $\gamma = 90° 21' \pm 10'$, $U = 383{\cdot}4$ Å^3; $D_m = 1{\cdot}71 \pm 0{\cdot}02$ (by flotation); $Z = 1$, $D_c = 1{\cdot}697$, $F(000) = 197{\cdot}98$. Space group $P\bar{1}$ (C_i^1, No. 2) from morphology and structure determination. Intensities of 1739 reflections were collected from six layers taken about the *a* axis, and five layers taken about the *b* axis, to give a set of 1248 independent reflections above background (*ca.* 72% of those possible with Cu-K_α radiation).

Bis(ω-nitroacetophenonato)-(2-methylpyridine)copper(II). [Cu(ω-nap)$_2$(α-pic)], (2), $C_{22}H_{19}CuN_3O_6$, $M = 484{\cdot}956$, Triclinic, $a = 10{\cdot}537 \pm 0{\cdot}01$, $b = 8{\cdot}624 \pm 0{\cdot}01$, $c = 12{\cdot}089 \pm 0{\cdot}01$ Å, $\alpha = 93° 18' \pm 10'$, $\beta = 94° 20' \pm 10'$, $\gamma = 92° 21' \pm 10'$, $U = 1093$ Å^3, $D_m = 1{\cdot}47 \pm 0{\cdot}02$ (by flotation), $Z = 2$, $D_c = 1{\cdot}474$, $F(000) = 481{\cdot}96$. Space group $P\bar{1}$ (C_i^1, No. 2) from morphology and structure determination. Intensities of 2563 reflections were collected from four

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[4] D. Attanasio, I. Collamati, and C. Ercolani, *J. Chem. Soc.* (*A*), 1971, 2516.

[5] I. Collamati and C. Ercolani, *J. Chem. Soc.* (*A*), 1971, 2522.

[6] M. Bonamico, I. Collamati, C. Ercolani, G. Dessy, and D. J. Machin, *Chem. Comm.*, 1967, 654.

[7] M. Bonamico and G. Dessy, *Chem. Comm.*, **1970**, 1218.

[8] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33**, (II A), 1113.

[9] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[10] J. S. Rollett and R. A. Sparks, *Acta Cryst.*, **1960**, **13**, 273.

layers taken about the *a* axis and seven layers taken about the *b* axis, to give 2066 independent reflections above the film background (*ca.* 41% of those possible with Cu-K_α radiation).

TABLE 2

Co-ordinates ($\times 10^4$) and temperature factors,* with standard deviations in parentheses, for [Cu(ω-nap)$_2$(α-pic)], (2)

	x/*a*	*y*/*b*	*z*/*c*	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cu	2235(1)	3779(2)	1237(1)	92(1)	23(3)	32(2)	103(2)	6(2)	44(1)
O(1)	2712(7)	2801(8)	−115(5)	135(8)	11(16)	78(10)	113(10)	20(11)	56(4)
O(2)	2728(7)	5828(8)	740(5)	144(8)	17(17)	69(10)	121(10)	3(12)	59(4)
O(3)	3785(8)	7480(9)	−145(6)	131(8)	38(18)	29(12)	105(10)	17(14)	101(6)
O(4)	1557(7)	4915(8)	2473(5)	97(6)	60(16)	33(9)	158(11)	17(12)	55(4)
O(5)	3943(6)	3574(9)	2312(5)	89(6)	69(16)	35(9)	168(11)	7(12)	60(4)
O(6)	5106(7)	3649(9)	3841(6)	105(7)	88(17)	25(11)	168(12)	12(14)	82(5)
N(1)	3411(7)	6111(9)	−88(7)	79(7)	26(18)	18(11)	96(11)	8(14)	73(6)
N(2)	4102(7)	3975(9)	3329(6)	84(7)	4(17)	20(10)	105(11)	1(13)	52(5)
N(3)	1424(8)	1755(9)	1533(6)	91(7)	9(17)	45(10)	104(11)	6(12)	46(4)
C(1)	3697(9)	5002(11)	−850(8)	74(8)	2(20)	36(12)	100(13)	5(15)	63(6)
C(2)	3340(9)	3428(12)	−868(7)	66(8)	11(21)	15(12)	116(14)	15(16)	61(6)
C(3)	3741(9)	2361(11)	−1749(7)	86(9)	1(21)	11(13)	99(13)	8(15)	53(5)
C(4)	3881(10)	801(12)	−1564(8)	91(9)	11(22)	24(14)	97(13)	27(17)	76(7)
C(5)	4248(11)	−237(14)	−2367(9)	107(11)	69(27)	22(16)	164(18)	21(21)	76(8)
C(6)	4469(12)	302(15)	−3417(10)	140(13)	4(29)	75(17)	160(18)	39(21)	85(8)
C(7)	4300(12)	1840(15)	−3621(9)	155(13)	11(31)	98(16)	184(20)	8(21)	70(7)
C(8)	3966(11)	2881(14)	−2824(8)	119(11)	4(27)	29(14)	159(17)	50(17)	54(6)
C(9)	3251(9)	4820(12)	3891(7)	96(10)	44(23)	36(13)	129(15)	12(16)	52(6)
C(10)	2062(9)	5171(11)	3435(7)	92(9)	18(22)	28(12)	109(14)	2(15)	45(5)
C(11)	1319(9)	6277(12)	4181(7)	95(9)	46(22)	40(12)	119(14)	9(15)	48(5)
C(12)	28(10)	6307(13)	3960(8)	97(10)	10(24)	33(14)	138(16)	20(18)	65(6)
C(13)	−697(11)	7255(15)	4619(9)	110(11)	67(28)	82(15)	193(20)	44(22)	82(8)
C(14)	−126)12)	8181(15)	5500(9)	152(13)	151(29)	51(17)	199(20)	4(22)	70(7)
C(15)	1179(13)	8152(15)	5734(9)	164(15)	83(33)	27(19)	208(21)	53(22)	68(8)
C(16)	1884(11)	7203(13)	5079(9)	113(11)	70(26)	51(16)	148(17)	30(20)	81(8)
C(17)	2167(13)	571(14)	1766(9)	169(15)	26(31)	38(17)	163(18)	75(18)	62(7)
C(18)	1747(13)	−896(14)	1852(11)	175(15)	37(31)	132(20)	123(17)	5(23)	121(10)
C(19)	514(16)	−1288(16)	1763(11)	253(20)	81(37)	131(23)	138(19)	5(24)	101(10)
C(20)	−303(13)	−79(18)	1563(11)	154(14)	205(30)	63(20)	238(26)	6(28)	110(11)
C(21)	151(10)	1541(14)	1420(7)	105(10)	26(26)	58(12)	189(19)	11(18)	48(5)
C(22)	−666(12)	2768(19)	1180(13)	109(12)	171(32)	66(23)	294(28)	1(36)	151(14)
				B/Å^2					
H(1)	4215	5342	−1460	4·00					
H(4)	3708	423	−821	4·00					
H(5)	4356	−1352	−2211	4·00					
H(6)	4748	−430	−4014	4·00					
H(7)	4428	2197	−4379	4·00					
H(8)	3878	3998	−2984	4·00					
H(9)	3506	5204	4676	4·00					
B(12)	−401	5645	3322	4·00					
H(13)	−1640	7261	4449	4·00					
H(14)	−648	8865	5964	4·00					
H(15)	1609	8812	6372	4·00					
H(16)	2825	7182	5256	4·00					
H(17)	3106	805	1884	4·00					
H(18)	2376	−1715	1986	4·00					
H(19)	187	−2380	1834	4·00					
H(20)	−1244	−306	1521	4·00					

* See footnote to Table 1.

Bis(ω-*nitroacetophenonato*)*bis*-(4-*methylpyridine*)*copper*(II). [Cu(ω-nap)$_2$(γ-pic)$_2$], (3), $C_{28}H_{26}CuN_4O_6$, $M = 578{\cdot}085$, Monoclinic, $a = 19{\cdot}238 \pm 0{\cdot}010$, $b = 9{\cdot}268 \pm 0{\cdot}005$, $c = 17{\cdot}710 \pm 0{\cdot}010$ Å, $\beta = 120° 5' \pm 5'$, $U = 2732$ Å^3, $D_m = 1{\cdot}41 \pm 0{\cdot}02$ (by flotation), $Z = 4$, $D_c = 1{\cdot}405$, $F(000) = 1107{\cdot}4$. Space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences and structure determination. Intensities of 2591 reflections were collected from eight layers taken about the *b* axis, and seven layers about the *c* axis, to give 1983 independent reflections above background (*ca.* 62% of those possible with Cu-K_α radiation).

Determination and Refinement of the Structures.—In (1) the special Cu atom position (centre) was chosen as the origin (0,0,0), in (2) the copper atom position was found from a three-dimensional Patterson synthesis, and in (3), since there are eight general equivalent positions in the space group, the four molecules must each possess a centre of symmetry or a two-fold axis. It is possible to arrange the ligands around the copper atom so as to confer either a centre of symmetry or a two-fold axis on the molecule. The interpretation of the Patterson synthesis indicates that the special Cu atom position is in a centre of symmetry, which was chosen as the origin (0,0,0). For each structure the co-ordinates of all other atoms, except hydrogen, were found by Fourier syntheses. At this stage *R* was 0·21 for (1), 0·20 for (2), and 0·23 for (3). For each structure five cycles of 4 × 4 block-diagonal least-squares refinement of non-hydrogen atomic positional and thermal parameters were performed, the function minimized being $\Sigma w(|F_o| - k|F_c|)^2$. Weights were assigned to the reflections according to the function $w = (A + B|F_o| + CF_o^2)^{-1}$ with $A = 1{\cdot}50$, $B = 1{\cdot}00$, and $C = 0{\cdot}020$ for (1),

TABLE 3

Co-ordinates ($\times 10^4$) and temperature factors,* with standard deviations in parentheses, for $[\mathrm{Cu}(\omega\text{-nap})_2(\gamma\text{-pic})_2]$, (3)

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cu	0(0)	0(0)	0(0)	28(0)	1(1)	10(1)	125(2)	13(1)	16(0)
O(1)	1002(2)	−261(4)	1144(2)	28(1)	−13(4)	8(2)	137(6)	18(4)	19(1)
O(2)	−376(2)	−2035(5)	393(2)	41(2)	−51(5)	17(2)	148(6)	−15(5)	21(1)
O(3)	−632(3)	−3066(5)	1311(3)	41(2)	−68(6)	41(3)	166(6)	−33(6)	37(2)
N(1)	−188(2)	−2291(5)	1166(3)	28(1)	2(5)	21(3)	102(6)	−18(5)	26(2)
N(2)	−481(3)	1200(5)	564(3)	30(2)	3(5)	18(3)	130(7)	1(5)	20(2)
C(1)	509(3)	−1782(6)	1863(3)	26(2)	3(5)	16(3)	111(7)	3(6)	25(2)
C(2)	1072(3)	−879(5)	1810(3)	26(2)	18(5)	12(3)	98(6)	11(5)	17(2)
C(3)	1850(3)	−651(6)	2649(3)	24(1)	12(5)	15(3)	105(7)	−2(6)	23(2)
C(4)	2351(3)	465(7)	2692(4)	34(2)	−29(7)	20(4)	130(7)	8(7)	33(2)
C(5)	3089(4)	664(8)	3439(4)	34(2)	−49(8)	23(4)	183(11)	−17(9)	43(3)
C(6)	3338(3)	−235(8)	4136(4)	25(2)	−13(7)	−1(3)	197(11)	−11(8)	34(2)
C(7)	2857(4)	−1344(8)	4106(4)	38(2)	27(8)	3(4)	155(10)	25(8)	32(2)
C(8)	2110(3)	−1552(7)	3365(4)	30(2)	0(6)	10(3)	116(7)	17(7)	32(2)
C(9)	−130(4)	2447(7)	976(4)	40(2)	−11(8)	33(4)	159(9)	−2(8)	34(2)
C(10)	−470(4)	3344(8)	1327(4)	51(3)	0(8)	45(5)	145(9)	−3(8)	39(3)
C(11)	−1203(4)	3005(8)	1249(4)	44(3)	45(8)	47(5)	149(9)	36(9)	45(3)
C(12)	−1561(4)	1707(8)	829(5)	42(3)	7(8)	49(5)	153(10)	16(9)	51(3)
C(13)	−1189(3)	869(8)	486(4)	32(2)	1(7)	33(4)	155(10)	13(8)	45(3)
C(14)	−1600(5)	3966(10)	1611(6)	65(4)	37(12)	91(8)	211(14)	−38(14)	84(5)

	x/a	y/b	z/c	B/Å^2
H(1)	628	−2078	2459	4·50
H(4)	2177	1127	2183	4·50
H(5)	3443	1476	3466	4·50
H(6)	3874	−83	4671	4·50
H(7)	3043	−2006	4617	4·50
H(8)	1757	−2358	3349	4·50
H(9)	394	2730	1029	4·50
H(10)	−184	4244	1639	4·50
H(12)	−2080	1387	777	4·50
H(13)	−1466	−30	163	4·50

* See footnote to Table 1.

A = 5·00, B = 1·00, and C = 0·0125 for (2), and A = 4·00, B = 1·00, and C = 0·005 for (3). The hydrogen atoms in calculated positions (assuming C–H bond lengths 1·09 Å and to complete tetrahedra around the carbon atoms) were introduced with approximately the isotropic temperature factors of the atoms to which they are linked. Attempts to locate the hydrogen atoms of the methyl groups of the α-pic and γ-pic molecules were unsuccessful. Two further isotropic least-squares cycles of refinement of only the positional and thermal parameters of non-hydrogen atoms were then performed. The R values were reduced by *ca.* 0·6%. At the end of isotropic refinement R was 0·14 (1), 0·13 (2), and 0·14 (3). The refinements were continued for non-hydrogen atoms, by use of anisotropic thermal parameters, until convergence was achieved. Five cycles [six for (2)] were necessary to give final shifts on the atomic parameters of $<0{\cdot}5\sigma$. The final R was 0·072 for (1), 0·096 for (2), and 0·072 for (3).

Tables 1—3 give the final atomic co-ordinates and the thermal vibration parameters of the crystal-chemical units. The structure factors based on the final atomic parameters, compared with the observed structure amplitudes, are listed in supplementary Publication No. SUP 20479 (11 pp., 1 microfiche).* Bond distances and angles within the formula units are reported with their estimated standard deviations in Tables 4—6.

Calculations.—Calculations were carried out on the IBM 7040 and UNIVAC 1108 computers of Rome University. Programmes used for calculation of intensity corrections, interlayer scaling, Wilson plots, Fourier syntheses, and interatomic distances and angles are described in ref. 11, for structure-factors and least-squares refinement in ref. 12, and calculation of least-square planes in ref. 13. Atomic scattering factors for hydrogen atoms were taken from ref. 14, and for the other atoms neutral atomic scattering factors,

TABLE 4

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for (1)

(*a*) Distances

Cu–O(1)	1·928(4)	C(2)–C(3)	1·482(6)
Cu–O(2)	1·931(5)	C(3)–C(4)	1·400(8)
Cu–O(3)	2·595(5)	C(3)–C(8)	1·409(10)
O(1)–C(2)	1·273(8)	C(4)–C(5)	1·385(8)
O(2)–N	1·311(7)	C(5)–C(6)	1·393(12)
O(3)–N	1·255(6)	C(6)–C(7)	1·395(11)
N–C(1)	1·352(6)	C(7)–C(8)	1·383(8)
C(1)–C(2)	1·410(7)		

(*b*) Angles

O(1)–Cu–O(2)	91·1(0·2)	N–C(1)–C(2)	124·0(0·6)
O(1)–Cu–O(3)	87·6(0·2)	C(1)–C(2)–C(3)	118·0(0·5)
O(2)–Cu–O(3)	97·6(0·2)	C(2)–C(3)–C(4)	119·0(0·6)
Cu–O(1)–C(2)	124·9(0·3)	C(2)–C(3)–C(8)	123·0(0·5)
Cu–O(2)–N	123·1(0·3)	C(3)–C(4)–C(5)	121·0(0·6)
O(1)–C(2)–C(1)	124·8(0·4)	C(3)–C(8)–C(7)	121·0(0·6)
O(1)–C(2)–C(3)	117·2(0·4)	C(4)–C(3)–C(8)	119·0(0·5)
O(2)–N–C(1)	123·8(0·5)	C(4)–C(5)–C(6)	120·0(0·6)
O(2)–N–O(3)	116·8(0·4)	C(5)–C(6)–C(7)	120·0(0·6)
O(3)–N–C(1)	119·4(0·5)	C(6)–C(7)–C(8)	120·0(0·8)

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[11] A. Domenicano and A. Vaciago, unpublished work.

[12] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[13] R. Spagna, unpublished work.

[14] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

TABLE 5

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for (2)

(*a*) Distances

Cu–O(1)	1·907(7)	C(3)–C(8)	1·432(14)
Cu–O(2)	1·961(7)	C(4)–C(5)	1·371(15)
Cu–O(4)	1·937(7)	C(5)–C(6)	1·409(17)
Cu–O(5)	2·158(6)	C(6)–C(7)	1·379(18)
Cu–N(3)	1·975(8)	C(7)–C(8)	1·355(16)
O(1)–C(2)	1·295(12)	C(9)–C(10)	1·382(13)
O(2)–N(1)	1·305(11)	C(10)–C(11)	1·551(13)
O(3)–N(1)	1·237(11)	C(11)–C(12)	1·368(14)
O(4)–C(10)	1·246(10)	C(11)–C(16)	1·391(16)
O(5)–N(2)	1·255(9)	C(12)–C(13)	1·398(14)
O(6)–N(2)	1·236(10)	C(13)–C(14)	1·378(16)
N(1)–C(1)	1·348(12)	C(14)–C(15)	1·384(18)
N(2)–C(9)	1·373(12)	C(15)–C(16)	1·383(17)
N(3)–C(17)	1·342(15)	C(17)–C(18)	1·335(17)
N(3)–C(21)	1·354(13)	C(18)–C(19)	1·32(2)
C(1)–C(2)	1·392(14)	C(19)–C(20)	1·40(2)
C(2)–C(3)	1·465(13)	C(20)–C(21)	1·39(2)
C(3)–C(4)	1·388(14)	C(21)–C(22)	1·50(2)

(*b*) Angles

O(1)–Cu–O(2)	90·6(0·3)	N(2)–C(9)–C(10)	124(0·8)
O(1)–Cu–O(4)	171·4(0·3)	N(3)–C(21)–C(20)	119(1·1)
O(1)–Cu–O(5)	101·0(0·3)	N(3)–C(21)–C(22)	116(1·0)
O(1)–Cu–N(3)	87·0(0·3)	N(3)–C(17)–C(18)	125(1·2)
O(2)–Cu–O(4)	85·7(0·3)	C(1)–C(2)–C(3)	120(0·8)
O(2)–Cu–O(5)	95·3(0·3)	C(2)–C(3)–C(4)	120(0·8)
O(2)–Cu–N(3)	168·3(0·3)	C(2)–C(3)–C(8)	121(0·9)
O(4)–Cu–O(5)	87·1(0·3)	C(3)–C(4)–C(5)	122(1·0)
O(4)–Cu–N(3)	95·0(0·3)	C(3)–C(8)–C(7)	119(1·1)
O(5)–Cu–N(3)	96·4(0·3)	C(4)–C(3)–C(8)	118(0·9)
Cu–O(1)–C(2)	127(0·6)	C(4)–C(5)–C(6)	119(1·1)
Cu–O(2)–N(1)	127(0·6)	C(5)–C(6)–C(7)	120(1·1)
Cu–O(4)–C(10)	128(0·6)	C(6)–C(7)–C(8)	122(1·1)
Cu–O(5)–N(2)	127(0·6)	C(9)–C(10)–C(11)	115(0·7)
Cu–N(3)–C(17)	119(0·8)	C(10)–C(11)–C(12)	118(0·8)
Cu–N(3)–C(21)	124(0·7)	C(10)–C(11)–C(16)	124(0·9)
O(1)–C(2)–C(1)	124(0·9)	C(11)–C(12)–C(13)	121(0·9)
O(1)–C(2)–C(3)	116(0·9)	C(11)–C(16)–C(15)	122(1·1)
O(2)–N(1)–O(3)	116(0·8)	C(12)–C(13)–C(14)	121(1·1)
O(2)–N(1)–C(1)	123(0·8)	C(12)–C(11)–C(16)	118(0·9)
O(3)–N(1)–C(1)	121(0·8)	C(13)–C(14)–C(15)	119(1·1)
O(4)–C(10)–C(9)	130(0·9)	C(14)–C(15)–C(16)	120(1·0)
O(4)–C(10)–C(11)	114(0·8)	C(17)–C(18)–C(19)	121(1·3)
O(5)–N(2)–O(6)	118(0·8)	C(17)–N(3)–C(21)	117(0·9)
O(5)–N(2)–C(9)	124(0·7)	C(18)–C(19)–C(20)	116(1·3)
O(6)–N(2)–C(9)	118(0·7)	C(19)–C(20)–C(21)	122(1·2)
N(1)–C(1)–C(2)	126(0·9)	C(20)–C(21)–C(22)	125(1·1)

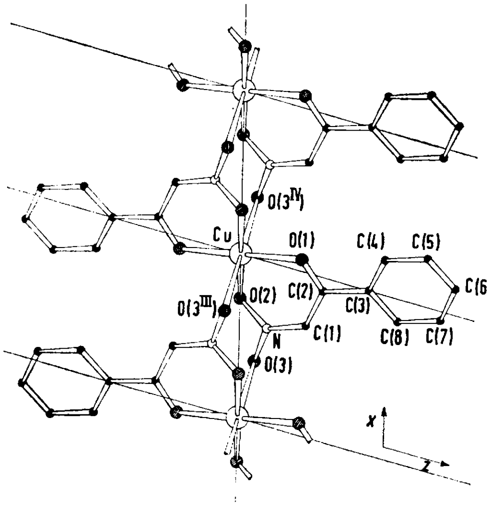

FIGURE 1 [010] Projection of the Cu(ω-nap)$_2$ structure (1) showing the polymeric system of complex molecules. Positions referring to the superscript are: (III) $-1-x, -y, -z$; (IV) $1+x, y, z$

corrected for anomalous dispersion in the case of Cu,[15] were taken from ref. 16.

Description of Structures.—Figure 1 shows the molecular structure and the crystal packing of the Cu(ω-nap)$_2$ complex (1) viewed along the *b* axis. The copper atom at the centre of symmetry requires a *trans*-planar molecular arrangement; by symmetry, the four oxygen atoms from the two ligands and the copper atom define a plane. Intermolecular interactions occur between the copper atom and the oxygen atoms (not otherwise involved in the chelation) of the nitro-groups of neighbouring molecules, thus completing the copper co-ordination sphere by a distorted octahedron of six oxygen atoms. The repetition of Cu–O interactions produces a polymeric system. The octahedral distortion is evident in the Cu–O(3^{III}) distance [2·595(5) Å], which is much greater than the Cu–O(1) and Cu–O(2) distances. Each nitro-ketonic group is slightly twisted (*ca.* 10°) around the C(1)–C(2) direction, the chelate ring is therefore approximately planar, the maximum and mean deviations being 0·066 and 0·042 Å respectively. The phenyl ring shows the expected planarity and is approximately coplanar with the chelate ring.

TABLE 6

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for (3)

(*a*) Distances

Cu–O(1)	1·991(3)	C(3)–C(4)	1·389(9)
Cu–O(2)	2·252(5)	C(3)–C(8)	1·385(8)
Cu–N(2)	2·004(5)	C(4)–C(5)	1·384(7)
O(1)–C(2)	1·256(6)	C(5)–C(6)	1·362(10)
O(2)–N(1)	1·250(6)	C(6)–C(7)	1·366(10)
O(3)–N(1)	1·237(7)	C(7)–C(8)	1·391(7)
N(1)–C(1)	1·374(5)	C(9)–C(10)	1·384(12)
N(2)–C(9)	1·353(8)	C(10)–C(11)	1·382(11)
N(2)–C(13)	1·335(9)	C(11)–C(12)	1·400(10)
C(1)–C(2)	1·407(8)	C(11)–C(14)	1·510(14)
C(2)–C(3)	1·504(5)	C(12)–C(13)	1·385(12)

(*b*) Angles

O(1)–Cu–O(2)	83·1(0·1)	C(2)–C(3)–C(8)	122·8(0·5)
O(1)–Cu–N(2)	90·8(0·2)	C(3)–C(8)–C(7)	120·5(0·6)
O(2)–Cu–N(2)	90·6(0·2)	C(3)–C(4)–C(5)	120·2(0·6)
Cu–O(1)–C(2)	127·2(0·3)	C(4)–C(3)–C(8)	118·5(0·4)
Cu–O(2)–N(1)	122·4(0·3)	C(4)–C(5)–C(6)	120·8(0·7)
Cu–N(2)–C(9)	120·8(0·5)	C(5)–C(6)–C(7)	120·0(0·5)
Cu–N(2)–C(13)	121·6(0·4)	C(6)–C(7)–C(8)	120·1(0·6)
O(1)–C(2)–C(1)	127·5(0·3)	N(2)–C(9)–C(10)	122·4(0·7)
O(1)–C(2)–C(3)	116·6(0·5)	N(2)–C(13)–C(12)	123·5(0·6)
O(2)–N(1)–O(3)	119·2(0·4)	C(9)–C(10)–C(11)	120·5(0·6)
O(2)–N(1)–C(1)	122·3(0·5)	C(9)–N(2)–C(13)	117·3(0·6)
O(3)–N(1)–C(1)	118·5(0·4)	C(10)–C(11)–C(12)	116·9(0·7)
N(1)–C(1)–C(2)	125·6(0·5)	C(10)–C(11)–C(14)	122·1(0·6)
C(1)–C(2)–C(3)	115·9(0·4)	C(11)–C(12)–C(13)	119·3(0·7)
C(2)–C(3)–C(4)	118·6(0·4)	C(12)–C(11)–C(14)	121·0(0·7)

Figure 2 shows the structure of the α-pic complex (2). The copper atom is five-co-ordinated with a tetragonal pyramidal arrangement. The oxygen atoms O(1), O(2), O(4) and the nitrogen atom N(3) from the α-pic molecule form an approximate square planar arrangement around the copper atom, which is slightly raised out of the mean plane (0·17 Å) towards the apical oxygen atom O(5). In the region of the sixth octahedral position a short contact of 3·1 Å occurs between the copper atom and the carbon atom C(22) of the methyl group of the α-pic molecule. The tetragonal distortion is evident in the Cu–O(5) bond length [2·158(6) Å] which is significantly greater than the basal

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[15] Don T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[16] Don T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

Cu–O and Cu–N bond distances (1·93 and 1·98 Å). The two ligand molecules are not equivalent. For one of these, chelation is on the basal plane of the pyramid; the slight differences in the two distances Cu–O(1) and Cu–O(2) (1·907 and 1·961 Å) could be accounted for by incomplete data reflections and neglected absorption. In the second ligand the oxygen atom O(4) is on the basal plane while the other occupies the apical position; the Cu–O(4) bond length is close to the other Cu–O basal distances and different from the Cu–O(5) bond distance [2·158(6) Å]. The oxygen, nitrogen, and carbon atoms in the chelate rings are essentially planar, the maximum and mean deviations being 0·025 and 0·013 Å respectively. In each ligand molecule the mean plane of the phenyl ring carbons makes an angle of *ca.* 25° (22 and 28°) with the mean chelate ring planes. The α-pic exhibits the expected planarity and the plane of this molecule is approximately perpendicular to the two planes of the nitro-ketonic groups. The bond lengths and angles within the α-pic ligand agree with accepted values.[17] A few rather short intermolecular contacts are found (3·3 and 3·5 Å) between oxygen atoms O(2), O(3), O(5), and O(6) and the carbon atoms of the neighbouring molecules. Apart from these rather close approaches the intermolecular distances are those predicted on the basis of van der Waals radii.

Figure 3 shows the structure of the bis-(γ-pic) addition complex (3). The centre of symmetry passes through the copper atom and requires a *trans*-octahedral arrangement. The equatorial co-ordination involves the O(1), O(1′), N(2), and N(2′) atoms while O(2) and O(2′) are in the apical positions. The octahedral distortion is evident in the Cu–O(2) bond length [2·252(5) Å] which is significantly greater than the equatorial Cu–O(1) [1·991(3) Å] and Cu–N(2) [2·004(5) Å] bond distances. The chelate ring is almost planar, the maximum and mean deviations being 0·050 and 0·038 Å; this plane is inclined at an angle of 21° to the phenyl ring plane. The γ-pic ligand exhibits the expected planarity; the plane of this ligand is approximately perpendicular to that of the nitro-ketonic group. Short intermolecular contacts (3·34 and 3·46 Å) are present between the oxygen atom O(3) (not involved in the chelation) and the carbon atoms C(1) and C(8) of a neighbouring molecule.

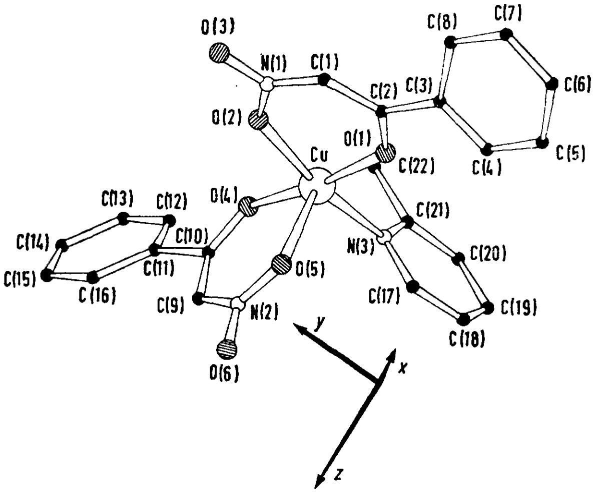

FIGURE 2 Molecule of [Cu(ω-nap)$_2$(α-pic)], (2)

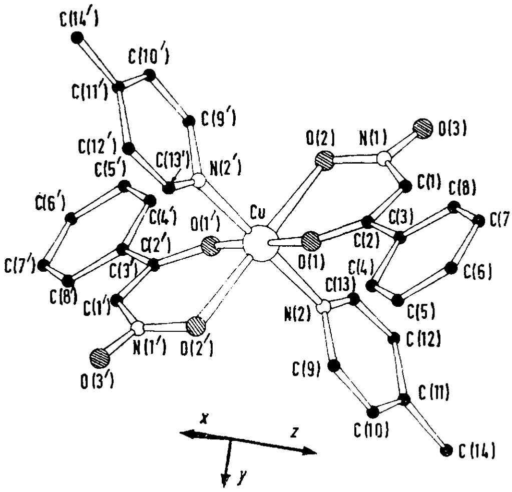

FIGURE 3 Molecule of [Cu(ω-nap)$_2$(γ-pic)$_2$], (3)

DISCUSSION

In the Cu(ω-nap)$_2$ complex (1) the co-ordinating properties of the nitro-group with respect to the copper atom are found to be very similar to those of the ketonic group. These Cu–O distances (and the other comparable bond lengths) appear to be analogous to those of the copper(II) complexes with β-diketones.[18] This confirms the increased co-ordinating ability of the nitro-group when it is conjugated to a carbonyl group. The Cu–O and Cu–N distances involved in square planar co-ordination to the copper atom in (2) and (3) are similar to those reported for other compounds with copper co-ordinated by both oxygen and nitrogen atoms.[19] In (2) the apical Cu–O(5) bond length [2·158(6) Å] is greater than the basal Cu–O distances. However it is shorter than any other of this kind [20] because the copper atom is slightly out of the mean basal plane. The Cu–O(2) bond distance [2·252(5) Å] in (3) is in agreement with that found in the bis(pyridine) adduct of bis(hexafluoroacetylacetonato)copper(II) [21] which provided the first example of Jahn–Teller distortion in a symmetrical ligand. For all three structures the bond lengths in the chelate rings are shorter than the single bond distances N–O, N–C, C–C, and C–O.[22] This implies that chelation to the metal by ω-nitroacetophenone occurs with the formation of a π electron resonating system, which extends through the metal on both ligand rings. The relative shortening of the C–O and C–C bonds in the chelate rings is analogous to that found in β-diketonates. In the Cu(ω-nap)$_2$ complex the approximate coplanarity of the phenyl and chelate rings may signify an inter-ring conjugation and at the same time an efficient crystal packing.

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[17] G. Davey and F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 2803.

[18] Ping-Kay Hon, C. E. Pluger, and R. Linn Belford, *Inorg. Chem.*, 1966, **5**, 516.

[19] G. E. Gurr, *Acta Cryst.*, 1968, **B24**, 1511 and references therein.

[20] G. W. Bushnell, *Canad. J. Chem.*, 1971, **49**, 555.

[21] M. V. Veidis, G. H. Schreiber, T. E. Gough, Gus J. Palenik, *J. Amer. Chem. Soc.*, 1969, 1859.

[22] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.

The slight twist of the two rings probably depends on the steric interference between the two hydrogen atoms H(1) and H(8). Such steric interference probably also causes the twist (*ca.* 10°) of the chelate ring about the C(1)–C(2) bond. This twist is not present in (2) and (3) since the phenyl and chelate rings make a bigger angle (21°). This is in agreement with the u.v. spectra[23] of the free ligand which suggest non-coplanarity of the phenyl and chelate rings.

In (2) the co-ordination of the N-base along the basal plane of the square pyramid causes the displacement of one of the oxygen atoms of a ligand molecule in the apical position and suggests the unusual feature that the situation for each of the two ligand molecules is different. One of these has the same co-ordination as in (1), while in the other Cu–O bond lengths are not equivalent. This is in agreement with the diffuse reflectance spectrum of this complex, which differs in shape and intensity from those observed for the other six-co-ordinate base addition complexes.[4]

In (3) the ligand molecules are analogous to the asymmetrical ligand of (2). In this complex the *trans*-equatorial co-ordination of the N-bases and the formation of two short equatorial and two long apical Cu–O bond lengths provides an interesting example of distortion of a ligand because of the Jahn–Teller effect in the copper(II) ion. The difference between the *trans*-configuration of this complex and that of the yellow form of the bis-adducts is determined by the substitution along the d_{z^2} metal orbitals of two nitrogen atoms by two oxygen atoms and in the reverse substitution in the equatorial plane.

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[2/501 *Received, 3rd March,* 1972]

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[23] M. Bossa, personal communication.