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Metal Complexes of the Deprotonated Form of *N,N'*-Bis(2'-pyridinecarboxamide 1'-oxide)-1,2-ethane, (enpco), a Dinegative N_2O_2 Quadridentate Pyridine *N*-Oxide Ligand. X-ray Crystal Structure of $[Cu(enpco\text{-}2H)]_2 \cdot 8H_2O$

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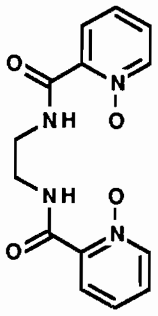
Abstract

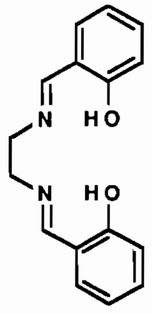
The magnetic properties and infrared and electronic spectra of nickel(II) and copper(II) complexes with deprotonated enpco are discussed. An X-ray structure analysis shows that the complex $[Cu(enpco\text{-}2H)]_2 \cdot 8H_2O$ is triclinic, $P\bar{1}$, with $a = 6.988(2)$, $b = 11.748(2)$, $c = 12.289(2)$ Å, $\alpha = 63.06(2)$, $\beta = 81.17(1)$, $\gamma = 73.02(2)°$ and $Z = 2$. The ligand $(enpco\text{-}2H)^{2-}$ coordinates as a distorted square-planar N_2O_2 donor via the deprotonated amide nitrogens and the *N*-oxide oxygens. An *N*-oxide oxygen from each $(enpco\text{-}2H)^{2-}$ ligand also coordinates to the copper in an adjacent Cu(enpco-2H) entity, the resulting Cu–O bond length being 2.916(2) Å. This produces a centrosymmetric dimeric structure with tetragonal pyramidal coordination to each copper. The bridging Cu–O interaction is compared with that in a series of Cu(salen) complexes (H_2salen is the Schiff base of salicylaldehyde and ethylenediamine).

Introduction

Metal complexes of dinegative quadridentate N_2O_2 ligands have been very extensively studied [1–3]. The most common examples involve Schiff bases of salicylaldehyde and β-diketones with diamines. These ligands usually produce distorted square-planar N_2O_2 coordination [1–3]. All examples of which we are aware involve negative donor oxygens. We have extended our work on multidentate ligands involving pyridine *N*-oxide [4–10] by studying metal complexes of the deprotonated form of *N,N'*-bis(2'-pyridinecarboxamide 1'-oxide)-1,2-ethane (**I**, enpco). The ligand, $(enpco\text{-}2H)^{2-}$, appears to be the first dinegative quadridentate N_2O_2 ligand involving neutral donor oxygens. This ligand is the *N*-oxide derivative of a bis-picolinamide ligand [11, 12]. Deprotonated bis-picolinamides act as N_4 donors, and have been extensively investigated by Stephens and Vagg [13].



(**I**, enpco)



(**II**, H_2salen)

Experimental

Preparations

enpco

Ethylenediamine (3.0 g, 0.050 mol) was added to a solution of ethyl 2-pyridinecarboxylate 1-oxide [14] (16.5 g, 0.099 mol) in absolute ethanol (80 ml) and left to stir for 2 h. The resulting white precipitate was collected and recrystallised from aqueous ethanol (80%) (23 g, 77%). *Anal.* Found: C, 55.5; H, 4.5; N, 18.5. Calc. for $C_{14}H_{14}N_4O_4$: C, 55.6; H, 4.7; N, 18.5%.

Ni(enpco-2H)

A hot solution of nickel(II) chloride hexahydrate (0.79 g, 3.3 mmol) in absolute ethanol (50 ml) was added to a stirred solution of enpco (1.0 g, 3.3 mmol) in absolute ethanol (50 ml) containing triethylamine (0.70 g, 6.9 mmol). The mixture turned dark red and a yellow–orange precipitate formed. The compound was filtered off and washed with absolute ethanol. The complex was recrystallised from n-butanol (500 ml), producing yellow–brown crystals (1.1 g, 93%). *Anal.* Found: C, 46.6; H, 3.2; N, 15.4. Calc. for $NiC_{14}H_{12}N_4O_4$: C, 46.8; H, 3.4; N, 15.6%.

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Cu(enpco-2H)

A hot solution of copper(II) chloride dihydrate (1.13 g, 6.6 mmol) in absolute ethanol (50 ml) was added to a stirred solution of enpco (2.0 g, 6.6 mmol) in absolute ethanol (50 ml) containing triethylamine (1.40 g, 13.8 mmol). The mixture turned violet and a precipitate formed. The compound was filtered off and washed with absolute ethanol. The complex was recrystallised from n-butanol (800 ml), yielding violet crystals (2.2 g, 91%). *Anal.* Found: C, 46.2; H, 3.3; N, 15.3. Calc. for $CuC_{14}H_{12}N_4O_4$: C, 46.2; H, 3.3; N, 15.4%.

Analyses and Physical Measurements

These were as previously described [5].

Crystallography

Crystals

Recrystallisation of Cu(enpco-2H) usually produced only violet needles of the anhydrous compound, unsuitable for X-ray analysis. However, on one occasion a few block-like crystals of $[Cu(enpco\text{-}2H)]_2 \cdot 8H_2O$ were also obtained, during slow evaporation of a chloroform solution of Cu(enpco-2H). Subsequent attempts to obtain further quantities of the hydrate, using chloroform, water, other solvents, and their mixtures, were unsuccessful.

Crystal data

$CuC_{14}H_{20}N_4O_8$, $M = 435.9$, triclinic, space group $P\bar{1}$, $a = 6.988(2)$, $b = 11.748(2)$, $c = 12.289(2)$ Å, $\alpha = 63.06(2)$, $\beta = 81.17(1)$, $\gamma = 73.02(2)°$, $U = 859.8(3)$ Å^3, $D_o = 1.67$, $D_c = 1.68$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo}) = 12.9$ cm^{-1}. Crystal size: an irregular crystal approximately 0.2 × 0.2 × 0.2 mm.

Structure determination

Intensities for 3014 reflections were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode, using graphite monochromatized molybdenum radiation (λ 0.7107 Å) and $2\theta_{max}$ of 50°. Data were corrected for absorption. A total of 2415 reflections with $I > 3\sigma(I)$ were considered observed.

The copper atom was located using the Patterson method. Fourier methods located the ligand non-hydrogen atoms which were refined with anisotropic thermal parameters. A difference Fourier located ligand hydrogen atoms and the four water oxygens. Refinement was then carried out using anisotropic thermal parameters for the non-hydrogen atoms and thermal parameters for hydrogens set equal to those of the atoms to which they are bonded. Refinement and difference Fouriers could only definitively locate three water hydrogens, and no unique connectivity could be implied. Final residuals R and R_w were 0.023 and 0.025. Reflection weights used were $1/\sigma^2(F_o)$, being derived from $\sigma(F_o^2) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [15]. Structure solution and refinement computations were on a Cyber 172 computer and used local programs and BLOCKLS, a local version of ORFLS [16].

Results and Discussion

The complexes Ni(enpco-2H) and Cu(enpco-2H), involving deprotonated ligand, were obtained using triethylamine as deprotonating agent.

Infrared spectra have been compared to those of related pyridine systems, in order to identify *N*-oxide bands. The ν(NO) and δ(NO) modes for the free ligand have been unequivocally assigned to strong bands at 1187 and 793 cm^{-1}, respectively. These bands are at *ca.* 30–40 cm^{-1} lower frequency than for most *N*-oxide ligands, and this may be due to hydrogen-bonding to the amide hydrogen [4–9, 17]. In support of this, the ν(NH) band occurs at 3121 cm^{-1}, well below the value of 3300 cm^{-1} in the related pyridine ligand [18]. This mode is absent in the deprotonated complexes.

Assignment of the *N*-oxide modes in the complexes is less certain, because of their more complex spectra. The ν(NO) mode is assigned to two strong bands at 1196 and 1173 cm^{-1} for Ni(enpco-2H) and to bands at 1193 and 1170 cm^{-1} for Cu(enpco-2H). These are similar to frequencies in some other *N*-oxide complexes [4–9, 17]. Likewise, the δ(NO) mode is assigned to bands at 859 and 788 cm^{-1} for Ni(enpco-2H), and at 850 and 790 cm^{-1} for Cu(enpco-2H). The occurrence of pairs of NO bands may be due to coupling effects, or to the two *N*-oxide groups in each ligand being in non-equivalent environments.

The nickel(II) complex, Ni(enpco-2H), is diamagnetic. This is in keeping with a square-planar N_2O_2 structure. Nickel(II) complexes with other dinegative N_2O_2 ligands are usually square-planar and diamagnetic [2]. The reflectance spectrum contains strong absorption commencing at *ca.* 17 000 cm^{-1} and extending to higher frequencies. This is consistent with low-spin nickel(II) [19].

The magnetic moment of the copper(II) complex, Cu(enpco-2H), is almost invariant with temperature, having values of 1.80 BM at 304 K and 1.79 BM at 89 K. This indicates that strong interaction is absent. The copper(II) complex is violet and has a d–d band in its reflectance spectrum at 19 000 cm^{-1}. At liquid nitrogen temperature the band occurs at 19 100 cm^{-1}, with a shoulder at *ca.* 16 900 cm^{-1}. Many copper(II) complexes with other quadridentate N_2O_2 ligands have square-planar structures, such complexes are often violet, and have a d–d band in the region 18 000–19 500 cm^{-1}, similar to that found for Cu(enpco-2H) [1–3, 20–28]. In some cases five-coordinate tetragonal pyramidal structures are produced, either by bridging interactions or by axial coordination involving other donor molecules. This tends to shift the absorption band to frequencies as much as *ca.* 2000 cm^{-1} lower than in related planar complexes and this is often accompanied by a change in colour from violet to green [2, 20, 26–29]. It appears, therefore, that there is planar coordination by the ligand in Cu(enpco-2H), and that any bridging axial interaction is relatively weak.

An X-ray structural study of the copper(II) complex was carried out. The crystal studied was a hydrated form of the compound obtained in bulk preparations. The dimeric structure, [Cu(enpco-2H)]$_2$·8H$_2$O, was established. The atom numbering scheme and a perspective diagram [30] of part of the structure are given in Figs. 1 and 2. Atomic parameters, bond length and selected bond angle data are given in Tables 1 and 2. The coordination geometry in the crystal structure is in agreement with the conclusions, drawn earlier, from the spectroscopic and magnetic properties of the complexes.

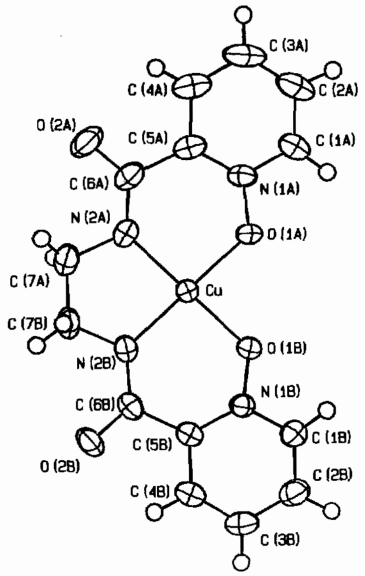

Fig. 1. The atom numbering scheme for the Cu(enpco-2H) entity.

The ligand (enpco-2H)$^{2-}$ coordinates as a distorted square-planar N$_2$O$_2$ donor via the deprotonated amide nitrogens and the *N*-oxide oxygens. An *N*-oxide oxygen, {O(1A) or O(1A)′}, from each (enpco-2H)$^{2-}$ ligand is also weakly bonded to the copper in an adjacent Cu(enpco-2H) entity, resulting in a centrosymmetric, dimeric structure. The coordination to the copper is tetragonal pyramidal, with the (enpco-2H)$^{2-}$ ligand in the basal plane. The basal N$_2$O$_2$ donor atoms deviate very slightly from their least-squares plane, by *ca.* ±0.03 Å in a tetrahedral distortion. The copper is very close to this plane, with a deviation of 0.02 Å towards the axial oxygen donor atom.

The Cu–N distances are 1.906(2) and 1.908(2) Å, similar to the Cu–N (amide) distances of 1.911–1.928(7) Å in the corresponding bis-picolinamide complex, which occurs in two crystallographically distinct molecules [11]. The Cu–O distances, within each Cu(enpco-2H) entity, are 1.913(1) and 1.918(1) Å to the bridging and non-bridging *N*-oxide oxygens, respectively. The out-of-plane bridging bond, linking the two Cu(enpco-2H) entities, is 2.916(2) Å. The bridging geometry, with in-plane and out-of-plane Cu–O bridging distances of 1.913(1) and 2.916(2) Å, respectively, appears to be the most distorted yet reported for an *N*-oxide-bridged copper(II) complex. Most *N*-oxide-bridged copper(II) complexes involve the metal halides and simple pyridine *N*-oxides [17]. These usually have tetragonal pyramidal coordination, but with both bridging Cu–O bonds in the basal plane. Distortions of the bridging geometry are small, in that the bridging Cu–O distances are *ca.* 1.9–2.2 Å [31, 32]. The copper(II) nitrate complexes [CuL$_2$(NO$_3$)$_2$]$_2$ (L = pyridine *N*-oxide or 4-methoxypyridine *N*-oxide) also have tetragonal pyramidal coordination, but one bridging Cu–O bond occupies an apical out-of-plane position. The in-plane and out-of-plane bridging Cu–O distances are

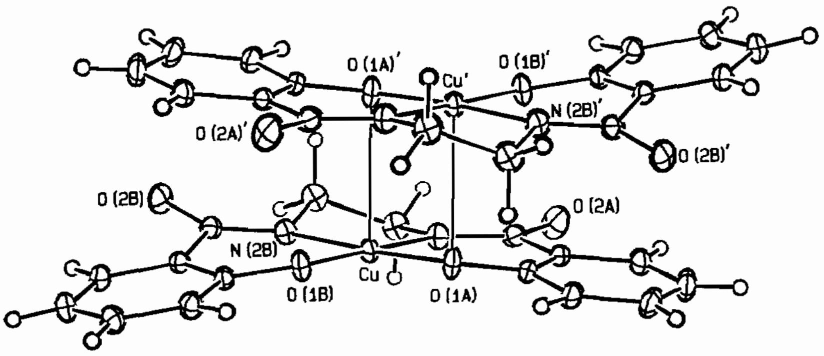

Fig. 2. A perspective drawing of the [Cu(enpco-2H)]$_2$ molecule.

TABLE I. Final Atomic Parameters and the Isotropic Equivalent of the Anisotropic Temperature Factor[a]

Atom	x/a	y/b	z/c	B_{eq}
Cu	0.2498(0)	0.0605(0)	0.4295(0)	2.21(1)
C(1A)	0.3263(3)	−0.1863(2)	0.7914(2)	3.16(7)
C(2A)	0.3343(4)	−0.3119(2)	0.8792(2)	4.08(8)
C(3A)	0.3307(4)	−0.4069(2)	0.8453(3)	4.53(9)
C(4A)	0.3128(3)	−0.3725(2)	0.7237(2)	3.74(8)
C(5A)	0.3001(3)	−0.2449(2)	0.6343(2)	2.74(6)
C(6A)	0.2644(3)	−0.2155(2)	0.5049(2)	2.98(1)
C(7A)	0.1766(4)	−0.0663(2)	0.2992(2)	3.46(8)
C(1B)	0.1789(3)	0.4326(2)	0.3961(2)	2.94(7)
C(2B)	0.1177(4)	0.5639(2)	0.3209(2)	3.43(7)
C(3B)	0.0723(4)	0.6020(2)	0.2017(2)	3.58(7)
C(4B)	0.0970(3)	0.5067(2)	0.1621(2)	3.03(6)
C(5B)	0.1616(3)	0.3730(2)	0.2383(2)	2.36(6)
C(6B)	0.1898(3)	0.2752(2)	0.1851(2)	2.50(6)
C(7B)	0.2258(3)	0.0596(2)	0.2049(2)	3.26(7)
N(1A)	0.3125(2)	−0.1550(2)	0.6723(1)	2.51(6)
N(2A)	0.2338(3)	−0.0943(2)	0.4205(2)	2.92(7)
N(1B)	0.1985(2)	0.3396(1)	0.3561(1)	2.24(6)
N(2B)	0.1976(3)	0.1519(2)	0.2593(1)	2.66(7)
O(1A)	0.3186(3)	−0.0302(1)	0.5980(1)	3.21(6)
O(2A)	0.2606(3)	−0.3136(2)	0.4898(2)	4.76(9)
O(1B)	0.2632(2)	0.2156(1)	0.4408(1)	2.96(7)
O(2B)	0.1989(3)	0.3235(2)	0.0709(1)	3.60(8)
OW(1)	0.2602(4)	0.1586(3)	0.7179(2)	6.83(8)
OW(2)	0.4191(4)	0.3704(3)	0.6582(3)	7.73(7)
OW(3)	0.5125(6)	−0.2370(4)	1.0832(3)	9.41(7)
OW(4)	0.2006(6)	−0.0142(4)	0.9602(3)	8.99(8)

[a] e.s.d.s given in parentheses.

1.968(5) and 2.439(6) Å, respectively, for the pyridine *N*-oxide complex and 1.940(6) and 2.578(5) Å, respectively, for the latter complex [31, 32].

The structures most closely related to [Cu(enpco-2H)]$_2$·8H$_2$O are those involving H$_2$salen (**II**), the Schiff base of salicylaldehyde and ethylenediamine. Our (enpco-2H)$^{2-}$ ligand differs in connectivity from salen^{2-} only by having a pyridine nitrogen and an amide oxygen in place of a phenol carbon and an aldimine hydrogen. Four structures have been reported for the copper(II)/salen^{2-} system, namely [Cu(salen)]$_2$, [Cu(salen)]$_2$·2CHCl$_3$, [Cu(salen)]·(NH$_2$)$_2$CS and [Cu(salen)]·*p*-NO$_2$C$_6$H$_4$OH [29, 20, 21, 23]. The first two complexes have centrosymmetric dimeric structures similar to that of [Cu(enpco-2H)]$_2$·8H$_2$O. The tendency to dimerisation decreases along the series in that the Cu–O out-of-plane bridging bond is 2.41 Å in [Cu(salen)]$_2$, 2.79 Å in [Cu(salen)]$_2$·2CHCl$_3$, and is absent in [Cu(salen)]·(NH$_2$)$_2$CS and [Cu(salen)]·*p*-NO$_2$C$_6$H$_4$OH, which are monomeric [29, 20, 21, 23]. In terms of dimerisation, [Cu(enpco-2H)]$_2$·8H$_2$O could be placed third in the above sequence, in that its Cu–O dimer bond length (2.916(2) Å) is slightly longer than that for [Cu(salen)]$_2$·2CHCl$_3$.

There is an approximate correlation between decreasing tendency to dimerisation in salen^{2-} complexes and increasing hydrogen bonding to ligand phenol oxygens. In [Cu(salen)]$_2$ hydrogen bonding is absent [29]. In [Cu(salen)]$_2$·2CHCl$_3$ each CHCl$_3$ is hydrogen-bonded to a non-bridging phenol oxygen, with a C–O distance of 3.03 Å (the van der Waals distance is 3.0 Å) [20, 33]. Similar hydrogen bonding occurs to both phenol oxygens in monomeric [Cu(salen)]·(NH$_2$)$_2$CS, the N–O distances being 2.89(1) and 2.94(1) Å (the van der Waals distance is 2.9 Å) [21, 33]. Stronger hydrogen bonding occurs to one ligand phenol oxygen in monomeric [Cu(salen)]·*p*-NO$_2$C$_6$H$_4$OH with an O–O distance of 2.65 Å (the van der Waals distance is 2.8 Å) [23, 33].

It is interesting that weak hydrogen bonding also appears to occur in [Cu(enpco-2H)]$_2$·8H$_2$O between the water oxygen OW(1) and both N-oxide oxygens. The OW(1)–O(1A) and OW(1)–O(1B) distances are 3.082(3) and 3.156(3) Å, respectively. Difference Fouriers during the course of the structure elucidation gave a peak in a position equidistant from O(1A) and O(1B) and approximately 1 Å from OW(1). This confirms the presence of at least some hydrogen bonding. The weak hydrogen bonding in [Cu(enpco-2H)]$_2$·8H$_2$O is consistent with the compound being structurally intermediate between [Cu(salen)]$_2$ and [Cu(salen)]·*p*-NO$_2$C$_6$H$_4$OH in terms of the extent of dimerisation. The OW(1) water and the remaining water molecules form a hydrogen-bonded network with O–O distances of 2.770–2.881(8) Å.

The ligand has an umbrella conformation [3]. The half-step distances (σ) from the copper to the planes of the pyridine rings involving N(1A) and N(1B) are 0.20 and 0.42 Å, respectively. The dihedral angles (α and β) [1] between the N$_2$O$_2$ donor plane and the two ONCCN chelate groupings {O(1A),N(1A), C(5A),C(6A),N(2A) and O(1B),N(1B),C(5B),C(6B), N(2B)} are 2.7° and 7.8°, respectively. The dihedral angle (γ) between the two chelate groupings is 9.5°. The umbrella conformation is accentuated by the two pyridine rings, involving N(1A) and N91B), which are tilted, respectively, by 6.0° and 5.8° with respect to their adjacent chelate groups, and are disposed at 15.5° relative to each other. The ethylenediamine linkage has a distorted gauche conformation. The N(2A)–C(7A)–C(7B)–N(2B) dihedral angle is 34.1(2)° and the deviations of C(7A) and C(7B) from the N$_2$O$_2$ donor plane are +0.11 and −0.39 Å, respectively.

Supplementary Material

All atom and thermal parameters and all interatomic angles and torsional angles, as well as structure factor listings, are available from the authors on request.

TABLE 2. Selected Bond Length (Å) and Bond Angle (°) Data[a]

Cu–O(1A)′	2.916(2)	N(2A)–C(7A)	1.466(3)
Cu–O(1A)	1.913(1)	N(1B)–C(1B)	1.355(3)
Cu–O(1B)	1.918(1)	N(1B)–C(5B)	1.363(2)
Cu–N(2A)	1.908(2)	N(2B)–C(6B)	1.306(3)
Cu–N(2B)	1.906(2)	N(2B)–C(7B)	1.467(3)
C(1A)–C(2A)	1.368(4)	O(1A)–N(1A)	1.341(2)
C(2A)–C(3A)	1.365(4)	O(1B)–N(1B)	1.340(2)
C(3A)–C(4A)	1.376(4)	O(2A)–C(6A)	1.255(3)
C(4A)–C(5A)	1.387(3)	O(2B)–C(6B)	1.252(2)
C(5A)–C(6A)	1.511(3)	OW(1)–O(1A)	3.082(3)
C(1B)–C(2B)	1.365(3)	OW(1)–O(1B)	3.156(3)
C(2B)–C(3B)	1.382(3)	OW(1)–OW(2)	2.770(4)
C(3B)–C(4B)	1.369(3)	OW(1)–OW(4)	2.792(4)
C(4B)–C(5B)	1.390(3)	OW(2)–O(2A)′	2.783(3)
C(5B)–C(6B)	1.514(3)	OW(2)–OW(3)″	2.881(5)
C(7A)–C(7B)	1.506(4)	OW(3)–O(2B)′	2.839(3)
N(1A)–C(1A)	1.349(3)	OW(3)–OW(4)	2.825(5)
N(1A)–C(5A)	1.361(3)	OW(4)–OW(4)‴	2.799(8)
N(2A)–C(6A)	1.304(3)	Cu–Cu′	3.737(0)
N(2A)–Cu–N(2B)	87.0(1)	O(1A)–Cu–O(1B)	85.3(1)
N(2A)–Cu–O(1A)	94.1(1)	N(2A)–Cu–O(1A)′	100.3(1)
N(2A)–Cu–O(1B)	179.1(2)	N(2B)–Cu–O(1A)′	95.9(1)
N(2B)–Cu–O(1A)	176.5(1)	O(1B)–Cu–O(1A)′	80.3(1)
N(2B)–Cu–O(1B)	93.6(1)	O(1A)–Cu–O(1A)′	80.7(1)

[a] The symbol X′ refers to the atom X at $1 - x, \bar{y}, 1 - z$, the symbol X″ refers to the atom X at $1 - x, \bar{y}, 2 - z$, and X‴ refers to the atom X at $\bar{x}, \bar{y}, 2 - z$.

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