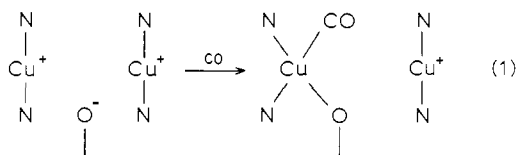


density to engage in binding an excellent  $\pi$  acid like CO. The reactivity of the previously characterized two-coordinate Cu(I) complex<sup>14</sup> with CO is likely a result of coordination from the other nitrogen donors of the ligand framework to the Cu(I) ions.<sup>20</sup>

While we cannot reject the notion that steric effects account for the observed binding of only one CO per binuclear copper unit in deoxy-Hc, we can provide an alternative explanation for the stoichiometry based on electronic effects. If each copper in deoxyhemocyanin were three-coordinate as previously suggested,<sup>8</sup> we would expect that each copper ion would bind CO in a tetra-coordinate fashion by analogy with simple copper carbonyls,<sup>19</sup> and one would observe a 1:1 ratio of CO/Cu. Similarly, if each copper is statically two-coordinate, we should expect deoxy-Hc to be inert to carbon monoxide. However, if one of the two-coordinate copper ions binds an additional ligand and becomes three-coordinate, then the observed 1:2 stoichiometry obtains. If one accepts the notion that there is ample space for each copper to bind a molecule of CO,<sup>22</sup> our results provide indirect evidence that each copper in deoxy-Hc is substantially two-coordinate but that one copper is able to bind an additional donor in the presence of CO.

While the possibility exists that a third endogenous N donor is near one of the copper centers,<sup>23</sup> another notion is that the bridging ligand accepts that role (see eq 1). Binding of the O



donor to only one of the copper ions leaves the other copper two-coordinate, hence unreactive toward CO. Unfortunately, we have not been able to generate a species with the [CuN<sub>2</sub>(OR)CO] coordination unit, thus we do not know if such a species can even exist or what its properties will be; work toward that goal is in progress.

**Acknowledgment.** This work was supported by Grant No. CHE-7817324 from the National Science Foundation. We thank Professor Derek J. Hodgson and his group for their generous assistance with the X-ray crystallographic studies.

**Registry No.** 1, 81028-65-1; 2, 81028-23-1; CO, 630-08-0; 3,5-dimethylpyrazole, 67-51-6;  $\alpha,\alpha'$ -dibromo-*m*-xylene, 626-15-3.

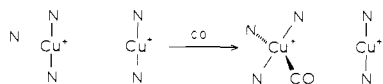
**Supplementary Material Available:** Table S1 listing positional and thermal parameters for [Cu(xypz)]<sub>2</sub>[BF<sub>4</sub>]<sub>2</sub> and a figure showing the atom numbering scheme for the [Cu(xypz)]<sub>2</sub><sup>2+</sup> cation (3 pages). Ordering information is given on any current masthead page.

(20) The validity of this statement is suggested by a recent paper<sup>21</sup> that reports the isolation of a bis(carbonylcopper(I)) adduct whose ligand is structurally identical with the one reported by Reedijk.<sup>14</sup> The copper in the former complex is in an N<sub>3</sub>(CO) coordination environment.

(21) Gagné, R. R.; Kreh, R. P.; Dodge, J. A.; Marsh, R. E.; McCool, J. *Inorg. Chem.* 1982, 21, 254-261.

(22) EXAFS data<sup>7b</sup> suggest that the copper atoms are >5 Å apart; therefore, there should be enough space to form a bis(carbonyl) adduct.

(23) EXAFS measurements are not very sensitive for detecting a low-Z atom at a large distance from the metal site, and hence a weakly bound ligand may have been missed.<sup>7b</sup> Since the two coppers appear to be identical in the deoxy form,<sup>10</sup> a third donor near one of the coppers would have to have little influence on the EXAFS measurements yet be near enough to coordinate when CO is present.



Reedijk's complex<sup>14</sup> may be the closest mimic for this type of behavior since the aliphatic nitrogen does not bind in the "deoxy" form, yet it apparently can when CO is added.<sup>20</sup>

## Hg<sup>+</sup> (6s<sup>1</sup>) Ions in KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>: New Paramagnetic Probes of Cationic Dynamics Near Phase Transitions in Hydrogen-Bonded Ferroelectrics and Antiferroelectrics

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We present here electron paramagnetic resonance (EPR) evidence to show that Hg<sup>+</sup> ions can be substituted for K<sup>+</sup> in KH<sub>2</sub>PO<sub>4</sub> (a hydrogen-bonded ferroelectric) and for NH<sub>4</sub><sup>+</sup> ions in NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (a hydrogen-bonded antiferroelectric<sup>1</sup>). This study was undertaken because, while the (solid-solid) structural phase transitions in these compounds have been considered as models of structural and ferroelectric/antiferroelectric phase transitions, the microscopic details of their own transition mechanisms are not yet understood.<sup>2</sup> Current theoretical models of structural phase transitions need data on the low-frequency ( $\sim 10^8$ – $10^{11}$  Hz) motion as well as the higher frequency lattice vibrations. The low-frequency motion falls in the domain where EPR spectroscopy is most effective for studying motional effects. Consequently, EPR spectroscopy has been extensively used for studying the dynamics of the anions (PO<sub>4</sub><sup>3-</sup>) as well as the cations (K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, etc.) in the KH<sub>2</sub>PO<sub>4</sub>-type compounds.<sup>2</sup> In using the EPR technique for studying these (diamagnetic) compounds, of course, it has been necessary to introduce a suitable paramagnetic ion (or free radical) into their lattices. We noticed that the probes used for studying the role of the cations K<sup>+</sup>, Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, etc., were Cr<sup>3+</sup> (3d<sup>3</sup>), Fe<sup>3+</sup> (3d<sup>5</sup>), Cu<sup>2+</sup> (3d<sup>9</sup>), and Tl<sup>2+</sup> (6s<sup>1</sup>) ions. It is thus seen that all these probes have one or two units of positive charge higher than that of the alkali cation they are supposed to replace. Because of this extra charge, these ionic probes would exhibit a local electrostatic potential different from that of the substituted cations. Thus the local dynamic and structural properties seen by the probe would be expected to be different from that of the original lattice. We, therefore, searched for a monovalent paramagnetic ion and have found that Hg<sup>+</sup> (6s<sup>1</sup>) ions might represent such a probe.

The Hg(I) ions were incorporated into KH<sub>2</sub>PO<sub>4</sub> or NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> by doping these compounds with Hg(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O (5% by weight), growing single crystals from aqueous solution, and  $\gamma$  irradiating the doped crystals with a 500-Ci source for a few hours (exact time not critical). The crystals turned yellowish after  $\gamma$  irradiation, an indication that Hg<sup>+</sup> centers had been formed, as reported earlier<sup>3,4</sup> for Hg<sup>+</sup> in Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O doped with Hg(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O.

EPR measurements were made at X-band frequencies by using a Varian E-3 spectrometer. The microwave frequency was measured with a Hewlett-Packard 5345 L digital frequency counter, and the resonance fields were measured relative to the standard free-radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH). So that the spin Hamiltonian parameters could be determined, the variation of the EPR signals was investigated in the three mutually orthogonal crystal planes *ab*, *bc*, and *ca* of the tetragonal (*I*4<sub>2</sub>*d*) phases of KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>.<sup>1</sup> The crystallographic axes were easily identified by noting that these crystals grow as "bricks" with the *c* axis as the longest direction. The *a* and *b* axes are parallel to the orthogonal edges of the crystals.

Figure 1 shows typical EPR signals from single crystals of KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> at *T* = 300 K for  $\vec{H} // c$ , where  $\vec{H}$  is the externally applied (Zeeman) magnetic field. The spectra at other

(1) For a detailed discussion of ferroelectricity and antiferroelectricity, see M. E. Line and A. M. Glass, "Principles and Applications of Ferroelectrics and Related Materials", Clarendon Press, Oxford, England, 1977.

(2) See, for example, R. Blinc in "Magnetic Resonance of Phase Transitions", F. J. Owens, C. P. Poole, Jr., and H. A. Farach, Eds., Academic Press, New York, 1979, Chapter V.

(3) R. S. Eachus and F. G. Herring, *Can. J. Chem.*, 49, 2868 (1971).

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Table I. Spin Hamiltonian Parameters for Hg<sup>+</sup> Centers for KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub><sup>a</sup>

host	T, K	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$	$^{199}\text{A}_{\parallel}$ , MHz	$^{199}\text{A}_{\perp}$ , MHz	$\text{A}^{\text{S}}$ , MHz	ref
KH <sub>2</sub> PO <sub>4</sub>	300	1.9965 ± 0.0004	1.9972 ± 0.0004	1.9965 ± 0.0005	34 174 ± 6	34 940 ± 6	13.4 ± 0.5	this work
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	300	1.9959 ± 0.0005	1.9950 ± 0.0005	1.9959 ± 0.0005	33 944 ± 6	33 973 ± 6	13.0 ± 0.5	this work
Cd(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	300	1.9967 ± 0.0001	1.9900 ± 0.0001	1.9934 ± 0.0002	29 362 ± 1	29 127 ± 2		4

<sup>a</sup> The direction of  $g_{\parallel}$  and  $\text{A}_{\parallel}$  coincides with that of the crystallographic  $c$  axis. Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O is included for comparison.  $\text{A}^{\text{S}}$  is the superhyperfine coupling on each Hg<sup>+</sup> transition.

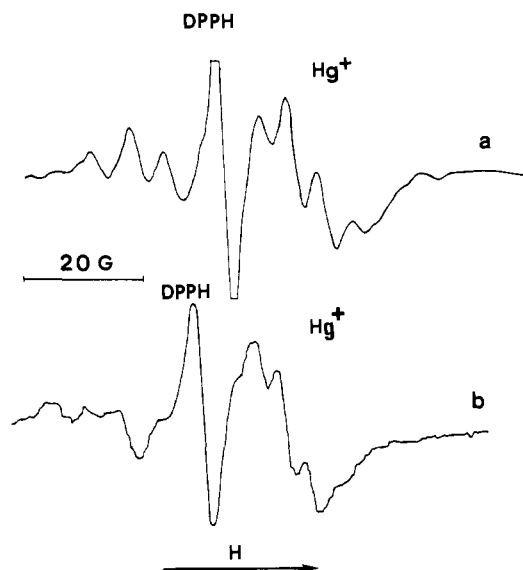


Figure 1. EPR spectra of the  $^{198,200}\text{Hg}^+$  center in KH<sub>2</sub>PO<sub>4</sub> (a) and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (b) for  $H//c$  at 300 K.

orientations were very similar. The angular variation of the signals was fitted to the spin Hamiltonian

$$\mathcal{H} = \beta \vec{H} \cdot \vec{g} \cdot \vec{S} + \vec{I}^{\text{Hg}} \cdot \vec{A}^{\text{Hg}} \cdot \vec{S} + \sum_{i=1}^4 \vec{I}_i^{\text{S}} \cdot \vec{A}_i^{\text{S}} \cdot \vec{S} \quad (1)$$

where  $\vec{g}$  is the electronic Zeeman tensor,  $S = 1/2$ ,  $\vec{I}^{\text{Hg}}$  is the nuclear spin of a Hg nucleus, and  $\vec{I}_i^{\text{S}}$  is the nuclear spin of the  $i$ th proton or phosphorus. The three terms in eq 1 are roughly responsible for the three distinct features in the spectra: (a) strong lines near 3400 G, (b) a weak satellite around 5400 G, and (c) the small ( $\sim 4$  G) splitting on both of these signals. Feature a is due to the electron Zeeman interaction of the most abundant, non-magnetic Hg isotopes ( $^{198,200}\text{Hg}$ ). Feature b is due to the hyperfine interaction of the electron spin with the  $^{199}\text{Hg}$  ( $I = 1/2$ ) isotope, and c is due to superhyperfine interaction of four (nearly) equivalent protons or phosphorus nuclei. The spin Hamiltonian parameters obtained are listed in Table I, which also contains data on Hg<sup>+</sup> ions in other hosts.

Comparison of the  $\vec{g}$ - and  $\vec{A}$ -tensor components of the center reported here with those of Hg(I) in Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O (cf. Table I) and the fact that the intensity of the observed signals is proportional to the amount of Hg(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O doped into KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> hosts strongly suggests that the center reported here is a Hg<sup>+</sup> ( $6s^1$ ) ion. That the lines around 3400 and 5400 G belong to the same center is proved by the observation that the intensity of the 5400 G line is  $\sim 10\%$  of that of the former, corresponding to the isotropic abundance ratio of  $^{200}\text{Hg}$  and  $^{199}\text{Hg}$ , and that both lines have virtually identical superhyperfine structure. This superhyperfine structure, better resolved for NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, is a 1:4:6:4:1 quintet which can be ascribed to the splitting from four equivalent  $I = 1/2$  nuclei. This quintet superhyperfine splitting changed to a 1:2:1 triplet at 148 K, the phase transition temperature of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, for  $H//c$ , as shown in Figure 2. This observation is somewhat analogous to the quintet-triplet proton superhyperfine splitting in the EPR spectra of the AsO<sub>4</sub><sup>3-</sup> centers in KH<sub>2</sub>AsO<sub>4</sub>, and in KH<sub>2</sub>PO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> doped with KH<sub>2</sub>AsO<sub>4</sub>.<sup>5,6</sup> It is noted that these earlier studies<sup>5,6</sup>

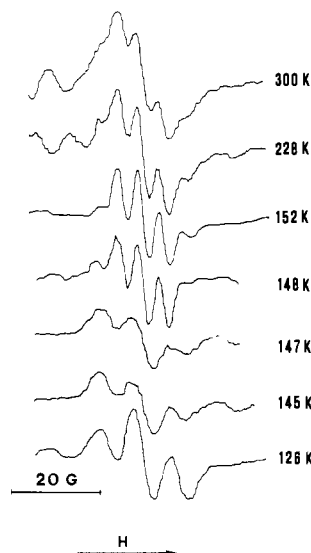


Figure 2. Temperature dependence of the quintet-triplet superhyperfine structure on the  $^{199}\text{Hg}^+$  hyperfine line in NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> for  $H//c$ . Note the change in the line shape below 148 K, the phase-transition temperature.

have yielded important dynamical data on the role of protons and the anions in causing the ferroelectric transition. The present results imply that the Hg<sup>+</sup> center is a potential tool for elucidating the ordering and hence the role of the cations in the phase-transition mechanism.

The hyperfine transition from the  $^{201}\text{Hg}$  ( $I = 3/2$ ) isotope is expected<sup>4</sup> to occur around 6700 G, which is outside the range of our E-3 spectrometer. However, the evidence presented above is believed to be sufficient for showing that the paramagnetic center is indeed a Hg<sup>+</sup> ion.

The near isotropic symmetry of the observed  $\vec{g}$  tensor,  $^{199}\text{Hg}$  hyperfine coupling, and even the quintet superhyperfine structure shows that the Hg<sup>+</sup> ion is located at a site of  $S_4$  point symmetry of the  $I42d$  space group of the KH<sub>2</sub>PO<sub>4</sub>-type crystals. This result indicates that perhaps Hg<sup>+</sup> ions substitute the K<sup>+</sup> (or NH<sub>4</sub><sup>+</sup>) ions without appreciable local distortion of the host lattice. Further interpretation of the definite site position and the nature of the superhyperfine structure could be obtained from studies on KD<sub>2</sub>PO<sub>4</sub>, ND<sub>4</sub>D<sub>2</sub>PO<sub>4</sub>, and other crystals (such as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, CsH<sub>2</sub>PO<sub>4</sub>, RbH<sub>2</sub>PO<sub>4</sub>, KH<sub>2</sub>AsO<sub>4</sub>, NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub>, and their deuterated analogues). Although such studies are currently in progress in our laboratory, the results reported here should stimulate research by others interested in understanding the role of cations and the central peak phenomenon<sup>5,7</sup> in the phase-transition behavior of these compounds. This is the first time that a paramagnetic probe has been found that has the same charge and local site symmetry as that of the host. Detailed ENDOR studies will be useful for further investigating the structure of this probe and to extend the time scale of EPR, as was done for the AsO<sub>4</sub><sup>4-</sup>, CrO<sub>4</sub><sup>3-</sup>, and SeO<sub>4</sub><sup>3-</sup> centers.<sup>4-6</sup>

It is noted, however, that since Hg<sup>+</sup> is a much heavier ion than the replaced ion (K<sup>+</sup> or NH<sub>4</sub><sup>+</sup>), the actual dynamics observed via Hg<sup>+</sup> might be somewhat different. Detailed studies are underway to investigate this question.<sup>8</sup>

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**Acknowledgment.** This research was supported in part by a grant from the WVU Energy Research Center.

**Registry No.** Hg<sup>+</sup>, 22542-11-6; KH<sub>2</sub>PO<sub>4</sub>, 7778-77-0; NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 7722-76-1.

(8) We thank a referee for suggesting this point.

## [2.2.1]Propellane

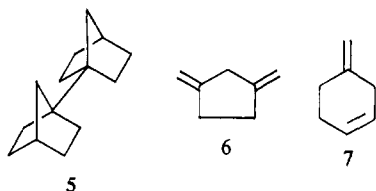
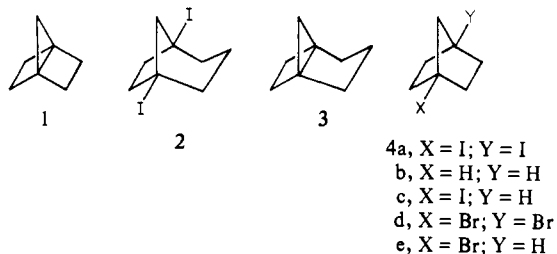
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Because of an inverted geometry at the bridgehead carbons<sup>1,2</sup> and a consequent unusual degree of reactivity, small strained-ring propellanes have generated considerable recent interest both from theoretical and synthetic points of view.<sup>3-10</sup> Much evidence for the transient existence of [2.2.1]propellane<sup>11</sup> (**1**) has been amassed



from both chemical and electrochemical reduction of 1,4-dihalonorbornanes,<sup>4c,10</sup> but attempts to isolate this compound have failed so far. We now report the preparation of matrix-isolated

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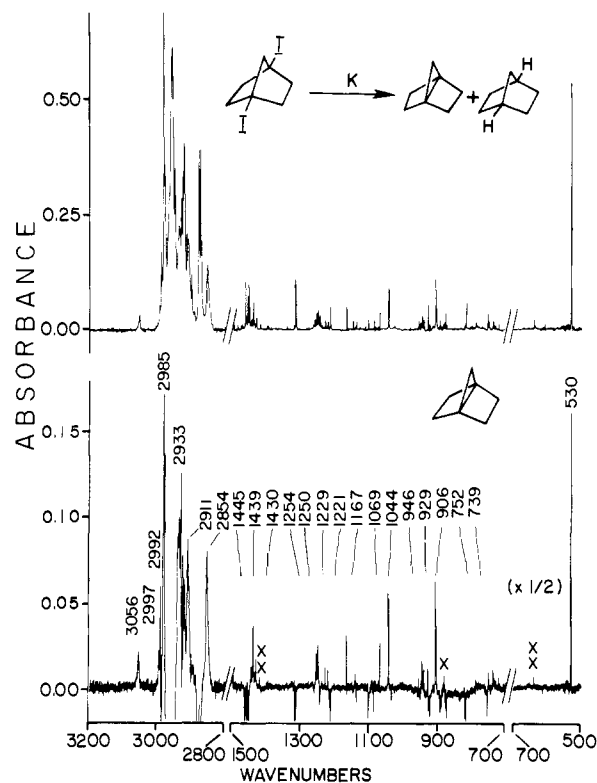
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(11) An alternative name for **1** is tricyclo[2.2.1.0<sup>1,4</sup>]heptane.



**Figure 1.** (Top) Matrix IR absorption spectrum (29 K) of the reaction products of **4a** with potassium at 120 °C in nitrogen. (Bottom) Matrix IR absorption spectrum of [2.2.1]propellane (29 K) with norbornane computer subtracted. More norbornane is subtracted than is actually present so the norbornane bands are now negative. The band marked X probably belongs to **6**. Those marked XX are unidentified. Note change of vertical scale below 700 cm<sup>-1</sup>.

**1** by the method of gas-phase dehalogenation with metal atoms<sup>12,13</sup> and its characterization by chemical and low-temperature spectroscopic means.

In the present version of the method,<sup>12b</sup> which developed from that described in ref 13, the vapor of the dihalide precursor in a sonicated stream of excess matrix gas is allowed to react with alkali metal vapor in a reaction cell (12 cm), whose extension reaches into an ultrasound cleaning bath, and is subsequently deposited on a cold CsI window. In this fashion, 1,3-diiodopropane yields cyclopropane and propene and 1,5-diiodobicyclo[3.2.1]octane<sup>4f</sup> (**2**) yields the known<sup>4</sup> [3.2.1]propellane (**3**).

Using 1,4-diiodobicyclo[2.2.1]heptane (**4a**)<sup>10a,14</sup> purified by preparative VPC (mp 103-104 °C), sonicated nitrogen carrier gas, and potassium vapor at 120 °C and trapping at 29 K, we obtained the FT IR matrix spectrum shown in Figure 1 (top). Comparison with authentic samples shows the presence of norbornane (**4b**) and another major component and the absence of significant amounts of 1-iodobicyclo[2.2.1]heptane<sup>15</sup> (**4c**), 1,1'-binorbornyl<sup>16</sup> (**5**), 1,3-dimethylenecyclopentane<sup>10a,17</sup> (**6**), and 4-methylenecyclohexene<sup>18,19</sup> (**7**).

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(17) The strongest band in **6** occurs at 883 cm<sup>-1</sup>, and the small band at 881 cm<sup>-1</sup> may be due to traces of this material.