cobalt ion in the thiocyanate complex (and quite likely the halide complexes) is thus CoO_3X_2. The strength of the bridging bonds is not excessive, since they break easily as the compound dissolves in dichloromethane and acetonitrile.[1] Since structures consistent with the observed stoichiometry could involve dimers, trimers, or heavier moieties, the exact stereochemistry can probably be determined only by X-ray diffraction.

(22) Most of the experimental work reported herein was performed at the University of Illinois and is abstracted from the Ph.D. thesis of D. W. Herlocker.

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Variation of the Oxygen Positional Parameter in Pyrochlores

Sir:

In a recent article Sleight[1] reported on three ternary oxides of mercury with the composition $A_2B_2O_7$ and the pyrochlore-type structure (space group Fd3m). He discussed the several possible choices of origin in the pyrochlore cell and listed (his Table IV) values of the oxygen positional parameter and metal–oxygen bond lengths which have been reported for 12 compounds. The observed range in the oxygen parameter, x = 0.305–0.355,[2] is stated to be "significantly different from an incorrect range (x = 0.325–0.355) recently given by Hoekstra and Siegel."[3]

The difference in x may possibly be considered significant, since the amended range includes the value x = 0.3125 in which regular octahedra are formed about the B atoms of $A_2B_2O_7$, but it is not due to an "indiscriminate use of x parameters from various pyrochlores where different origins were used" as Sleight suggests. Of the 12 compounds listed in his Table IV two, $Cd_2Re_2O_7$[4] and $Cd_2Nb_2O_7$, have x parameters less than 0.3125, and the error limits given on $Cd_2Re_2O_7$ could put it on either side of the regular octahedral configuration. Cadmium niobate was studied by Jona, Shirane, and Pepinsky[5] and given an x parameter of 0.305 ± 0.003. Sleight indicated that this value was obtained with niobium at the origin of the unit cell. While Jona, *et al.*, made no definitive statement on this point, we believe that all evidence points to the fact that these authors placed O_I at the origin.

(1) Figure 2 of Jona, *et al.*,[5] illustrates the pyrochlore structure projected on the (110) plane. The legend refers to Nb and Cd ions at ($^1/_8$, $^1/_8$) positions. The metal ions are found at these locations only with O_I at the origin.

(2) In section IV (p 906) Jona, *et al.*,[5] reported that "general intensity relations can be explained very well by Cd and Nb positions as given by Bystroem." Bystroem[6] placed O_I at the origin.

(3) Bond lengths and ionic radii calculated with x = 0.305 and O_I at the origin are more reasonable than with B atoms at the origin. Niobium and tantalum are generally considered to have virtually identical ionic radii. (In fact, Sleight made this assumption in his compounds, $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$.) Bond lengths calculated for $Cd_2Nb_2O_7$ with x = 0.305 and niobium at the origin are Nb–O_{II} = 1.92 Å and Cd–O_{II} = 2.73 Å (not 2.67 Å as given by Sleight[1]). However, with x = 0.320 the bond lengths are Nb–O_{II} = 1.97 Å and Cd–O_{II} – 2.62 Å. Recent data for $Cd_2Ta_2O_7$ with x = 0.317 give Ta–O_{II} = 1.96 Å and Cd–O_{II} = 2.64 Å. It is apparent that significantly better agreement in calculated bond lengths is obtained with O_I at the origin. For these reasons we believe that the correct value for x in $Cd_2Nb_2O_7$ is 0.320 based on B_o as the origin and that only $Cd_2Re_2O_7$ requires any appreciable extension of the range in x beyond the approximate range given in our paper. We wish to emphasize, however, that new data may require a further revision in x sometime in the future.

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(1) A. W. Sleight, *Inorg. Chem.*, **7**, 1704 (1968).

(2) For the purposes of the following discussion, we will adopt Sleight's choice of origin (B_o).

(3) H. R. Hoekstra and S. Siegel, *Inorg. Chem.*, **7**, 141 (1968).

(4) P. C. Donahue, J. M. Longo, R. D. Rosenstein, and L. Katz, *ibid.*, **4**, 1152 (1965).

(5) F. Jona, G. Shirane, and R. Pepinsky, *Phys. Rev.*, **98**, 903 (1955).

(6) A. Bystroem, *Arkiv. Kemi Mineral. Geol.*, **18A**, No. 21 (1944).

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Reply to: "Variation of the Oxygen Positional Parameter in Pyrochlores"

Sir:

Recently I have disagreed with Hoekstra and Siegel (HS) concerning the range of the oxygen parameter in the pyrochlore structure.[1,2] Two examples of compounds ($Cd_2Nb_2O_7$ and $Cd_2Re_2O_7$) were given where the oxygen parameters were outside the range given by HS. In reply to HS,[3] I agree that it is very likely that the oxygen parameter for $Cd_2Nb_2O_7$ actually falls within the range that they had given. This means that the origin chosen by HS is not a center of symmetry, and although it seems preferable to choose the origin at a center of symmetry for a centrosymmetric structure, this practice has frequently not been followed for the pyrochlore structure.

In the case of $Cd_2Re_2O_7$ the origin was specifically stated;[4] thus, the range of the oxygen positional

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(1) A. W. Sleight, *Inorg. Chem.*, **7**, 1704 (1968).

(2) H. R. Hoekstra and S. Siegel, *ibid.*, **7**, 141 (1968).

(3) H. R. Hoekstra and S. Siegel, *ibid.*, **8**, 2039 (1969).

(4) P. C. Donohue, J. M. Longo, R. D. Rosenstein, and L. Katz, *ibid.*, **4**, 1152 (1965).

parameter which I gave is substantially correct. This amended range is particularly significant because it extends the range given by HS by slightly more than 50% and, more importantly, because this extended range encompasses the region of a regular octahedron around the B cation.

The following corrections should be made to Table IV of ref 1: A–O for $Cd_2Nb_2O_7$ should read 2.73 Å instead of 2.67 Å, A–O for $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ should read 2.61 Å as in Table III, and x for $La_2Zr_2O_7$ should read 0.332 instead of 0.322.

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