been estimated to lie about 12.3 kK or 1.5 V above the ${}^6A_{1g}$ ground state.[6] This excited state could be a powerful oxidant and might accept an electron from $Ru(bipy)_3{}^{2+}$ in the primary cage to form $Ru(bipy)_3{}^{3+}$ and Fe^{2+}. These products would, of course, be indistinguishable from those formed by direct electron transfer quenching.

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(7) For simplicity the individual steps leading from $*Ru(bipy)_3{}^{2+}$ and Fe^{3+} to $Ru(bipy)_3{}^{3+}|Fe^{2+}$ are not shown. This reaction presumably proceeds via the diffusion-controlled formation of an encounter complex $*Ru(bipy)_3{}^{2+}|Fe^{3+}$ which then undergoes intramolecular electron transfer to form $Ru(bipy)_3{}^{3+}|Fe^{2+}$. The rate constant for this reverse electron-transfer reaction is neglected compared to k_2.

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(13) This estimate of the amount of electron-transfer quenching includes any contribution to the steady-state concentrations of $Ru(bipy)_3{}^{3+}$ and Fe^{2+} arising from an energy transfer path (see footnote 5).

(14) The efficiency of the formation of $*Ru(bipy)_3{}^{2+}$ from the singlet charge-transfer state formed by the irradiation of $Ru(bipy)_3{}^{2+}$ in the charge-transfer band is close to unity: F. E. Lytle and D. M. Hercules, *J. Am. Chem. Soc.*, **91,** 253 (1969); J. N. Demas and G. A. Crosby, *ibid.*, **93,** 2841 (1971).

(15) We have measured potentials of ~100 mV in a photogalvanic cell utilizing the reversible $Ru(bipy)_3{}^{2+}$–Fe^{3+} system.

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Solid State Structure and Oxidation States in Bis(diphenylglyoximato)nickel and -palladium Iodides

Sir:

Partial oxidation of stacked, square-planar, d^8 transition metal complexes may represent an effective method of increasing the metal-metal interaction and anisotropic electron transport in one-dimensional solid state "chain" compounds.[1] The Krogmann salt, $K_2Pt(CN)_4Br_{0.30}\cdot 3\ H_2O$, is the most thoroughly studied prototype to date.[1,2] The complexes $M(dpg)_2I$, dpg = diphenylglyoximate ($(C_6H_5)_2C_2N_2O_2H^-$) and M = Ni, Pd,[3] which have moderately high electrical conductivity,[4] are potentially new examples of such compounds. Based principally upon indirect chemical evidence and limited photographic X-ray data, the form of the iodine has been assigned both as I_2 (metal unoxidized, i.e., a halogen charge-transfer complex[5]) and as I_3^- (metal partially oxidized, i.e., a triiodide chain compound[6]);[7] a priori, I^- is also conceivable.[8] Though the basic one-dimensional character of this material had been suggested,[7a] we thought it important to investigate the nature of the structure and oxidation states in greater detail. We report here structural and spectroscopic studies which unambiguously establish the structure and indicate that the nickel and palladium atoms have formal fractional oxidation states as in the Krogmann compound.

Crystals of $Ni(dpg)_2I$ suitable for diffraction were grown by very slow cooling of *o*-dichlorobenzene solutions containing an excess of iodine. The compound crystallizes in the tetragonal space group $D_{4h}{}^8$-$P4/ncc$ with four formula units of $Ni(dpg)_2I$ in a cell of dimensions a = 19.887 (4) and c = 6.542 (2) Å.[9] Intensity data were collected on a diffractometer using Mo Kα radiation. The structure was solved by direct methods and was refined by full-matrix, least-squares techniques to an R index on F_o of 0.092 for the 31 variables and 294 observations above background. A listing of positional and thermal parameters will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material. A view of the structure down the c axis is shown in Figure 1. The $Ni(dpg)_2$ units stack (staggered by 90°) at intervals of 3.271 (1) Å. The Ni-Ni distance is thus ca. 0.28 Å shorter than that of unoxidized $Ni(dpg)_2$ (3.547 Å),[10] but longer than that of $Ni(dmg)_2$ (3.25 Å)[11] and nickel metal (2.49 Å).[12] The crystallographically imposed coordination geometry about the Ni atom is distorted from planar D_{2h} (as in $Ni(dmg)_2$[11]) to D_2 symmetry, with coordinated N atoms displaced 0.16 (1) Å above or below the mean molecular plane. The Ni-N (1.86 (2) Å), N-C (1.30 (3) Å), N-O (1.34 (3) Å), and O-O (2.43 (4) Å) distances are not significantly different from those of $Ni(dmg)_2$.[11] The iodine atoms are found in chains, filling "tunnels" defined by the phenyl rings. The closest C(phenyl)-I (4.13 (3) Å) and H(phenyl)-I (3.40 (1) Å) contacts indicate only van der Waals' phenyl-iodine interaction. The Ni/I ratio in this compound is 1.012 ± 0.020, as determined from the refinement of the occupancy of the I atom. The I positions are equally spaced at one half the c axis length (3.271 (1) Å). The root-mean-square amplitudes of vibration of the iodine perpendicular to the chain are normal at 0.234 (4) Å but abnormally large parallel to the chain at 0.756 (11) Å. The large amplitude along the chain is a manifestation of disorder, the nature of which cannot be resolved from the X-ray data as a number of different models lead to the same electron density distribution. In particular, the presence of discrete I-I units (separation 2.72-2.75 Å)[13] or discrete I-I-I^- units (I-I separation ca.

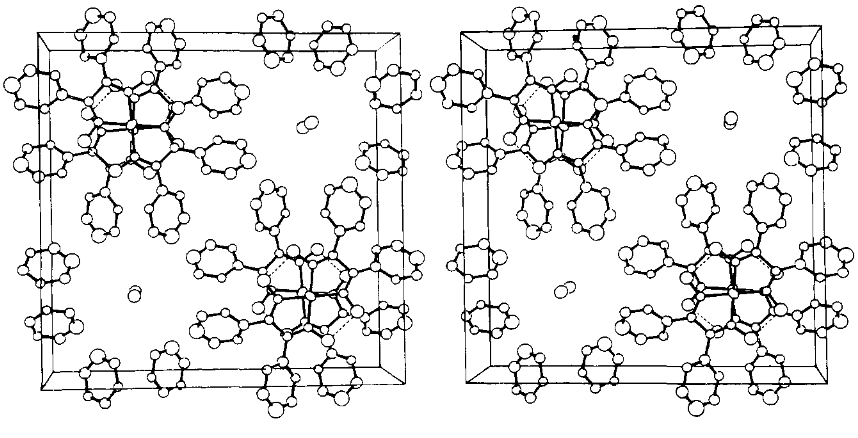

Figure 1. Stereoscopic view down the c axis of the unit cell of $Ni(dpg)_2I$, showing the channels surrounding the iodine chains. Dotted lines indicate the diphenylglyoximate O-H-O bonds. For all atoms, 50% probability thermal ellipsoids are shown; Ni and I were refined anisotropically.

2.8–3.1 Å)[6,14] cannot be discerned on the basis of the X-ray data. That the description of this disorder is inadequate presumably leads to the somewhat high R index.

It is possible to resolve the problem of oxidation states by other means. The Raman spectra of $Ni(dpg)_2I$ and $Pd(dpg)_2I$ (observed spinning with both Ar^+ and Kr^+ excitation) exhibit intense emissions at 160(vs) and 107(m) cm^{-1}. The bands are characteristic of ν_3 and ν_1 for I_3^- compounds,[15,16] and are not observed in the unoxidized complexes. There is no indication of I_2 ($\nu_{I-I} \approx$ 200–212 cm^{-1}).[5,17] Furthermore, ^{129}I Mössbauer spectra of $Ni(dpg)_2{}^{129}I$, to be discussed in detail elsewhere,[18] exhibit isomer shift and quadrupole splitting parameters which are in agreement with those of known I_3^- compounds,[19] and are incompatible with I^- or I_2.[19,20]

These results demonstrate that *all* members of the Ni, Pd, Pt group can form mixed valence compounds with the partial formal oxidation state of +2.3, that this can occur without metal–metal contacts as close as in the Krogmann salt, and that this can, in some cases, occur with ligands which are readily functionalized. Though the importance of the iodine chains for electron transport is not clear at present, the possibility that polyiodide chains themselves may represent a rational approach to the construction of electrically, magnetically, and optically one-dimensional materials merits further investigation.

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Supplementary Material Available. A table of positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-3545.

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Reaction of a Diphenylacetylene Complex of Cobalt with Isocyanide. A Novel Metalloring Formation

Sir:

Recently, metallocycles are drawing much attention for their important role both in catalytic and stoichiometric reactions.[1]

In this communication, we wish to report the synthesis of a series of cobalt metallocycles, which closely relates to the formation of diiminocyclobutenes and triiminocyclopentenes from isocyanide complexes of Ni and Co.[2]

One millimole of π-cyclopentadienyl-π-diphenylacetylenetriphenylphosphinecobalt[3] (**1**) reacted smoothly at 25° with 2 mmol of phenylisocyanide to give an air-stable orange crystalline compound with empirical formula $C_5H_5Co(PhC_2Ph)(PhNC)_2$ (**2a**). Similar compounds were obtained with 4-methylphenyl-, 2,6-dimethylphenyl-, and *tert*-butylisocyanide. The ir spectra of all of these compounds exhibit strong absorptions near 1700 cm^{-1} indicating the presence of exo-C═N double bonds in a strained ring.[4] From ir and NMR spectra, and the formalism of the inert gas rule, a structure has been suggested. A diiminocobaltacyclopentene ring with the C═C double bond coordinated to the central cobalt atom is proposed. The suggested structure was confirmed by X-ray crystallography.

Compound **2a** crystallized in space group Cc with unit cell dimensions a = 19.756 Å, b = 10.904 Å, c = 12.986 Å, and β = 114.43°; there are four molecules per unit cell. Intensity data were collected using monochromatic Mo Kα radiation on a Rigaku four-circle automatic diffractometer operating in the ω–2θ scan mode up to $2\theta \leq 60°$. Using 2741 independent reflections ($>3\sigma$), the structure was solved by the Patterson and Fourier methods and refined by block-matrix least-squares calculations to a discrepancy index of R = 0.058. The locations of all 25 hydrogen atoms were determined. As shown in Figure 1, the cobaltacyclopentene ring is highly bent to enable coordination of the double bond. The relevent bond lengths and angles are: Co-