with a considerable excess of the ammonium salt present in solution. $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$ is also obtained from dilute acid.

The chloride-deficient compounds, $M^I_3Mo_2Cl_7 \cdot 2H_2O$, are obtained from dilute acid to which alcohol is added. It is not obvious why the addition of alcohol causes this change in stoichiometry, nor is the structural nature of these new compounds yet known. A reasonable speculation is that they consist of chains of Mo_2Cl_8 groups sharing corners, in somewhat the way $ReCl_4$ consists of Re_2Cl_9 bioctahedra sharing corners.

All of the procedures used to prepare molybdenum(II) chloro complexes from $Mo_2(O_2CCH_3)_4$ have one thing in common: the solutions are at all times kept at or below 25°. Raising the temperature of such solutions causes oxidation to occur and this, when properly controlled, permits the preparation in good yield of compounds containing molybdenum in higher oxidation states. The oxidant (possibly H^+) has not been identified. Thus, when $Mo_2(O_2CCH_3)_4$ is dissolved in 12 *M* hydrochloric acid at 60°, the $Mo_2Cl_8{}^{3-}$ ion is formed[8] and can be isolated in essentially quantitative yield as the cesium salt or, in somewhat lower yield, as the rubidium salt. When concentrated HCl solutions of $Mo_2(O_2CCH_3)_4$ are boiled, the Mo(III) species $MoCl_5(H_2O)^{2-}$ and $MoCl_6{}^{3-}$ are formed.[11]

In conclusion we would emphasize that $Mo_2(O_2CCH_3)_4$ is a uniquely useful starting material for the preparation of many complexes of molybdenum in low or medium oxidation states. Thus, in addition to the $Mo_2Cl_8{}^{4-}$ ion, it affords excellent yields of $Mo_2Cl_8{}^{3-}$ which can then be converted essentially quantitatively to $Mo_2Cl_9{}^{3-}$ by electrolytic oxidation[8] and to species in still higher oxidation states by other oxidizing agents.[12]

CONTRIBUTION FROM THE MATERIALS GROUP, DEPARTMENT OF ENGINEERING SCIENCE,
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The Anti-Th_3P_4-Type Structure in the Lanthanum–Rhodium System: $La_4Rh_{\sim3}$[1]

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$La_4Rh_{\sim3}$ has the anti-Th_3P_4-type structure, with a = 8.922 (±3) Å. The space group is $I\bar{4}3d$-$T_d{}^6$. About $11^2/_3$ Rh atoms are randomly distributed in 12(a): $^3/_8$, 0, $^1/_4$. Sixteen La atoms are in 16(c): x, x, x, where x = 0.0570 (±5). The interatomic distances are: Rh–La, 2.851 (±5) and 3.357 (±4) Å; La–La, 3.591 (±7), 3.863 (±2), and 4.122 (±6) Å. The Rh atoms are not in contact with each other. The shortened Rh–La bond length, 2.851 Å, indicates some covalent bonding. The causes for the change in stoichiometry from A_3B_4 to A_4B_3, where A is always a transition element, and the variations in the positional parameter x between 0.057 and 0.083 are discussed in terms of the sizes and the chemical nature of the B atoms.

During the course of an investigation in the lanthanum–rhodium system,[2] an intermediate phase with a fairly simple X-ray diffraction pattern was found to exist in the vicinity of 42 atom % Rh. The alloys with 40, 41, and 42 atom % Rh were homogeneous in the as-cast state and consisted only of this phase. Figure 1 shows the microstructure of $La_{60}Rh_{40}$ in the as-cast state. It reveals a fine-grained (ASTM grain size number about 9) single-phase specimen. Similar microstructures were observed in the other alloys in the as-cast state. The alloy corresponding to the formula La_4Rh_3 (42.86 atom % Rh) was heterogeneous (two phased) in the as-cast state and was made up mostly of the phase found in the other alloys. The alloys were wrapped in thin molybdenum foils and annealed in evacuated quartz tubes. After annealing for 7 days at 900° under vacuum, the alloys with 40 and 41 atom % Rh also became heterogeneous and contained small amounts of an additional phase identified as La_5Rh_3. $La_{58}Rh_{42}$ remained single phased while the alloy with 42.86 atom % Rh showed small amounts of the next Rh-rich phase, La_5Rh_4, along with the phase found in the former.

Analysis of the microstructures and X-ray diffraction patterns of the above-mentioned alloys thus showed that an intermediate phase, whose structure is described in this paper, occurs at 42 atom % Rh and has a narrow-phase field, probably between 41.5 and 42.5 atom % Rh at 900° and perhaps between 40 and 42.5 atom % Rh at still higher temperatures. Since the arc-melted alloys were obtained with negligible weight loss (about 2 or 3 mg/g) during melting and there was no weight loss during annealing, a chemical analysis of the alloys was not deemed necessary. The assumed compositions correspond to the starting weights of La and Rh and are considered to be fairly accurate.

The powder X-ray diffraction pattern showed the phase to have a body-centered-cubic structure. The diffraction angles for Ni-filtered Cu Kα radiation were

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[1] Research supported by the sustaining research grant of the National Aeronautics and Space Administration (NASA) to the Louisiana State University, under Grant No. 19-001-024.

[2] P. P. Singh and A. Raman, *Trans. Met. Soc. AIME*, **245**, 1561 (1969).

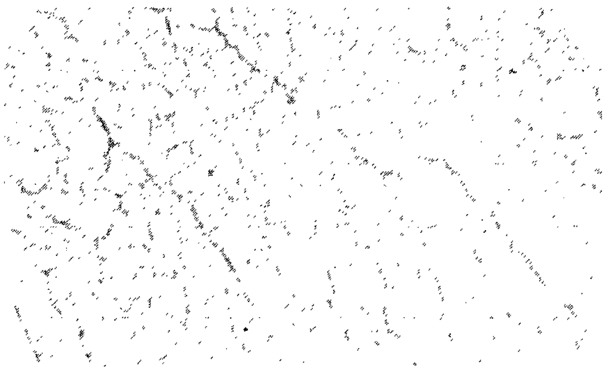

Figure 1.—The microstructure of $La_{60}Rh_{40}$ (as cast).

corrected for instrumental errors using semiconductor grade silicon (a_0 = 5.4199 Å) as the standard. The lattice parameters, calculated from the data of lines with $\sin^2 \theta$ less than 0.4, were plotted against the function $\cos^2 \theta/\sin \theta$ and extrapolated to the zero of this function employing the computer program HERTA 4 written by Vogel and Kempter.[3] The extrapolated lattice parameter is a = 8.922 (±3) Å. The length of the cell edge changes very slightly (less than 5 parts per thousand) with composition.

Each observed *hhl* reflection is of the kind $2h + l = 4n$. No other extinctions are noticeable except those corresponding to the body centering (*hkl* with $h + k + l = 2n + 1$ are absent). The volume of the unit cell is 710.3 Å^3. The mean atomic volume is 25.37 Å^3/atom, assuming 28 atoms per unit cell. This value fits well in the mean atomic volume curve for the system near 43 atom % Rh. It became apparent at this stage that the phase has an anti-Th_3P_4-type[4-6] structure.

The densities of the alloys with 40 and 42 atom % Rh were measured using crushed pieces. The surfaces of the chunks were made flat by grinding in order to minimize occluded and absorbed gases. Weighing was done in an electric balance to an accuracy of 10^{-4} g. The measured densities are 7.53 g/cm^3 for $La_{60}Rh_{40}$ and 7.85 g/cm^3 for $La_{58}Rh_{42}$. The density calculated from the X-ray data for the composition La_4Rh_3 (16 La and 12 Rh atoms) is 8.086 g/cm^3. Assuming atomic vacancies among the rhodium sites, the calculated densities are 8.006 g/cm^3 (with only $11^2/_3$ Rh atoms, 42.17 atom % Rh) and 7.765 g/cm^3 (with only $10^2/_3$ Rh atoms, 40 atom % Rh). Since the phase does not occur at the ideal stoichiometry and since the measured densities are low, it is postulated that some atomic vacancies (about $^1/_3$ to $^2/_3$ at 900° and possibly $^1/_3$ to $1^1/_3$ at still higher temperatures) occur randomly distributed at the sites of the set assigned to rhodium. The anti-Th_3P_4-type phase is designated as $La_4Rh_{\sim 3}$.

The Th_3P_4-type structure, first described by Meisel,[4] is now known to occur in several sulfides, selenides, tellurides, phosphides, arsenides, antimonides, bismuthides, and germanides of the rare earth and actinide elements. The stoichiometry is A_3B_4 in the rare earth phosphides, arsenides, and nontransition chalcogenides but switches to A_4B_3 in the antimonides, bismuthides, and germanides (A represents the rare earth elements). Vacancies in the structure were detected first in the rare earth sulfides by Zachariasen.[7] The range of composition of the isotypic phase in the Ce–S system extends from Ce_3S_4 to Ce_2S_3. An anomalous increase in the volume of the unit cell with $1^1/_3$ atomic vacancies for cerium was attributed by Zachariasen[7] to a variation in the nature of the chemical bond. At Ce_3S_4 the ionic bonding is presumed to be lost and more metallocovalent bonding prevails. Recently similar vacancies were found in the isotypic phase La_2Te_3.[8] No vacancies are reported, however, in the isotypic phases of the A_4B_3 stoichiometry.[6,9]

The Th_3P_4 structure is consistent with the space group $I\bar{4}3d$-T_d^6, with 12 Th atoms in 12 (a) ($^3/_8$, 0, $^1/_4$; etc.) and 16 P atoms in 16(c) (x, x, x; etc.).[10] In the anti-Th_3P_4-type structure the components switch places. The Rh atoms hence occupy the fixed, 12(a), positions and the La atoms are located at the sites 16(c) in the phase $La_4Rh_{\sim 3}$.

The parameter x for the La atoms was determined with the aid of intensity data obtained with crystal-monochromatized Cu Kα radiation in a Guinier–de Wolff powder camera. The photographs were extremely sharp and showed the weak lines, whereas diffractometer scans with either Cu Kα or Mo Kα radiations gave diffuse peaks and the extremely weak reflections were undetectable. Investigations with single crystals could not be undertaken due to lack of adequate facilities. The relative intensities, I_{obsd}, of the diffraction lines in the Guinier photograph of $La_{58}Rh_{42}$ (annealed) were estimated visually using a calibrated scale. The observed structure factor, $|F_o|$, is given by $[I_o/nLp]^{1/2}$, where n is the multiplicity factor, L is the Lorentz factor $1/(\sin 2\theta)(\sin \theta)$, p is the polarization factor $[1 + (\cos^2 2\theta)(\cos^2 2\alpha)]/(1 + \cos^2 2\alpha)$, θ is the diffraction angle for the plane (hkl) in the specimen, and α is the diffraction angle for X-rays in the quartz crystal of the monochromator. The intensities, given by the formula $I_c = |F_c|^2 nLp$, were calculated employing a computer program written by Jeitschko and Parthé.[11] An occupancy factor of 0.9722 ($^1/_3$ atomic vacancy) was assumed for the 12-fold Rh positions. No absorption corrections were made and the temperature parameters were assumed to be zero. The residual factor, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, was then calculated. The parameter x was refined by trial and error.

An initial value of x = 0.0645 was chosen (as was determined by La_4Ge_3 by Hohnke and Parthé[6]) and it was

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(3) R. E. Vogel and C. P. Kempter, "HERTA 4, Vogel–Kempter Lattice Parameter Program," Los Alamos Scientific Laboratory, Los Alamos, N. M.

(4) K. Meisel, *Z. Anorg. Allgem. Chem.*, **240**, 300 (1939).

(5) Strukturbericht 7, p 15.

(6) D. Hohnke and E. Parthé, *Acta Cryst.*, **21**, 435 (1966).

(7) W. H. Zachariasen, *ibid.*, **2**, 57 (1949).

(8) W. L. Cox, H. Steinfink, and W. F. Bradley, *Inorg. Chem.*, **5**, 318 (1966).

(9) F. Holtzberg, T. R. McGuire, S. Methfessel, and J. S. Suits, *J. Appl. Phys.*, **35**, 1033 (1964).

(10) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1959, p 329.

(11) W. Jeitschko and E. Parthé, "A Fortran IV Program for the Intensity Calculations of Powder Patterns," Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa.

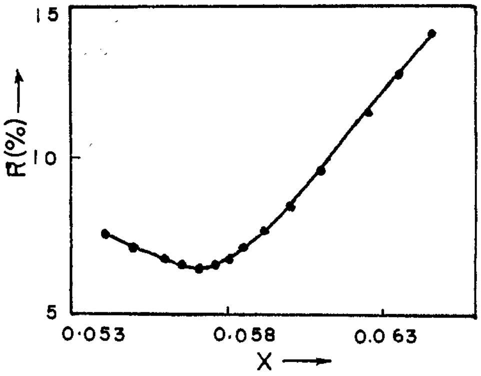

Figure 2.—Variation of the residual factor, R, with x.

then varied in steps of 0.0005 on either side of this value. The residual, R, was found to reach a minimum value of 0.067 for $x = 0.0570$. A plot of R vs. x is shown in Figure 2. The final refined value of x is considered to be accurate to ±0.0005. An indexed powder pattern of $La_4Rh_{\sim 3}$ is presented in Table I, which also contains the F_o and F_c values.

TABLE I

POWDER X-RAY DIFFRACTION PATTERN OF $La_4Rh_{\sim 3}$[a]

(hkl)	$10^3 \sin^2 \theta$ Obsd	$10^3 \sin^2 \theta$ Calcd	$\vert F_o \vert$	$\vert F_c \vert$
(211)	44.84	44.63	4.1	12.0
(220)	59.68	59.53	156.5	133.9
(310)	74.41	74.45	260.3	260.8
(321)	104.23	104.28	153.5	153.4
(400)	118.95	119.20	97.5	103.0
(420)	148.92	149.04	135.7	113.8
(332)	163.88	163.96	143.9	139.0
(422)	178.67	178.88	145.7	147.4
(510) (431)[c]	193.75	193.81	157.9	145.1
(521)	223.60	223.66	99.3	91.6
(611) (532)[c]	283.25	283.37	154.3	146.8
(620)	298.23	298.30	165.9	155.4
(541)	313.43	313.23	142.8	135.6
(444)	358.41	358.02	301.2	276.7
(633)[b] (721) (552)[c]	404.00	403.10	153.5	145.0
(642)[b]	420.23	418.00	116.9	132.6

[a] Alloy: $La_{58}Rh_{42}$, Guinier photograph with Cu Kα. [b] These lines were omitted for the extrapolation of the lattice constant. [c] $|F_o|$ and $|F_c|$ for these overlapping lines were obtained by adding the intensities of the individual lines and multiplying $[\Sigma I_o]^{1/2}$ and $[\Sigma I_c]^{1/2}$ by $[1/(\Sigma n)Lp]^{1/2}$.

Each Rh atom is surrounded by eight La atoms in dodecahedral coordination. An alternate description is to say that four of these La atoms form an elongated tetrahedron and the other four a rather flattened one, as is shown in Figure 3. The Rh–La distances are the same within each tetrahedron. There are, hence, two distinct Rh–La bond distances. For a value of $x = {}^1/_{12}$ (0.0833) the two tetrahedra would be regular and both A–B bond lengths would be equal. Each La atom is shared among three polyhedra and is surrounded by six Rh atoms. The Rh atoms are not in contact with each other.

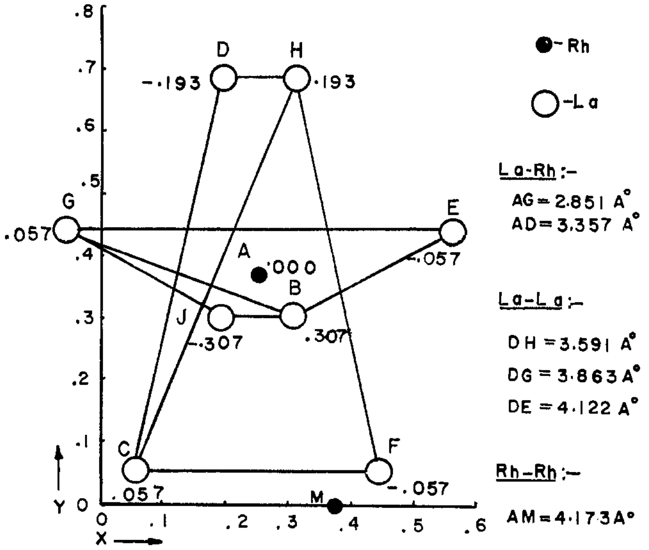

Figure 3.—Distorted tetrahedra of the La atoms around a central Rh atom situated at $^1/_4$, $^3/_8$, 0. The projection is on the (001) plane and the positional parameters z of the atoms are given. The parameters x and y can be inferred from the figure.

The following bond lengths are observed: La–Rh, 2.851 (±5) and 3.357 (±4) Å; La–La, 3.591 (±7), 3.863 (±2), and 4.122 (±6) Å. The shortest Rh–Rh distance is 4.173 (±2) Å.

As compared to the radii for 12-fold coordination of 1.87 and 1.34 Å for La and Rh, respectively, given by Pauling,[12] one of the Rh–La distances is considerably shortened while the other is slightly extended. It is felt that covalent bonding prevails between the central Rh atom and the four La atoms at a distance of 2.851 Å whereas essentially metallocovalent bonding exists between the same Rh atom and the other four La atoms. The La–La distance in the same tetrahedron is shortened whereas it is elongated between the La atoms of adjacent tetrahedra.

TABLE II

LATTICE CONSTANTS AND x PARAMETERS OF SOME ISOTYPIC PHASES

Phase, A_3B_4 or A_4B_3	Lattice parameter, a, Å	Positional parameter, x	Radius of B component atom, Å
La_3Se_4[c]	9.05[a]	0.075[b]	1.40
Gd_2Se_3 (with Gd vacancies)[c]	8.718	0.0715[b]	1.40
La_2Te_3[d]	9.619	0.0748[b]	1.60
La_4Ge_3[e]	9.356	0.0645	1.444
$La_4Rh_{\sim 3}$ (with Rh vacancies)[f]	8.922	0.057	1.342

[a] Value obtained from M. Guittard, Mm. A. Benacerraf, and J. Flahaut, *Ann. Chim.*, **9**, 25 (1964). [b] Determined from intensity data obtained using single crystals. [c] F. Holtzberg, Y. Okaya, and N. Stemple, Abstracts of the American Crystallographic Association Gatlinburg Meeting, 1965 (quoted in ref 8). [d] See ref 8. [e] See ref 6. [f] Present work.

The Th_3P_4-type structure seems to occur at the A_3B_4 stoichiometry when the B component atoms are strongly bound by covalent bonds in the elemental state. At this stoichiometry the atoms of the transi-

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(12) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

tion elements occupy the centers of the tetrahedra. As the B component becomes more and more metallic, the inverted stoichiometry A_4B_3 seems to be preferred and the atoms of the B component take over the central positions.

The occurrence of this structure with B component atoms having atomic radii ranging from 1.27 (S) to 1.66 (Sb) Å indicates that the sizes of these atoms do not influence the choice or the stability of the structure. However, the variations in the positional parameter x, represented in Table II, can be interpreted in terms of the variations in size. In the case of the A_3B_4 phases it appears that the parameter is not affected by the size of the B component atoms. (Compare the values for La_2Te_3 and La_3Se_4.) However, in the A_4B_3 phases it decreases with a decrease in the size of the B component atoms. (Compare the values for La_4Ge_3 and $La_4Rh_{\sim 3}$.)

$La_4Rh_{\sim 3}$ is the first representative of the Th_3P_4-type structure wherein both the component atoms are of transition elements. This structure has not yet been found in other rare earth–rhodium alloys.

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The Crystal and Molecular Structure of Tris(tetra-*n*-butylammonium) Octacyanomolybdate(V)

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The crystal and molecular structure of the tetra-*n*-butylammonium salt of the paramagnetic complex $Mo(CN)_8^{3-}$ has been determined by single-crystal X-ray diffraction methods and its electron spin resonance has been reexamined in light of the structural results. Intensity data were collected by counter techniques and the structure has been refined by least-squares methods to a conventional R factor of 0.094 for 597 nonzero independent reflections. The complex crystallizes in space group P4/ncc of the tetragonal system in a cell of dimensions a = 17.009 (5) Å, c = 22.784 (21) Å, and V = 6592 Å^3. An experimental density of 1.03 (4) g/cm^3 agrees with a calculated value of 1.03 g/cm^3 for Z = 4. The $Mo(CN)_8^{3-}$ anion possesses a slightly distorted triangular dodecahedral coordination geometry and is crystallographically required to have D_2 molecular symmetry. The two independent Mo–C bond distances do not differ significantly and have an average value of 2.12 (2) Å. Other important anion distances are the average C–N and Mo–N distances of 1.16 (2) and 3.27 (2) Å, respectively. The tetra-*n*-butylammonium cations exhibit significant disorder in the γ- and δ-carbon atoms of the butyl chains. The electron spin resonance spectrum of a polycrystalline sample of $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ has an isotropic g value of 1.991 ± 0.002 which agrees exactly with other values of $\langle g \rangle$ obtained from solution spectra or calculated from frozen-glass spectra. It is concluded that the $Mo(CN)_8^{3-}$ anion probably has the distorted dodecahedral coordination of D_2 symmetry in the solution state as well as in the crystalline state and that the unpaired electron occupies a metal-based orbital which has both $d_{x^2-y^2}$ and d_{z^2} character.

Introduction

There has been much discussion in the literature during the past decade concerning the geometry of discrete eight-coordination in transition metal complexes.[1-4] Particular attention in this area has been focused on the two octacyanomolybdate anions $Mo^{IV}(CN)_8^{4-}$ and $Mo^{V}(CN)_8^{3-}$. Recently, the crystal and molecular structure of $K_4[Mo(CN)_8]\cdot 2H_2O$, which was first reported 1939,[5] has been reinvestigated.[4] The triangular dodecahedral coordination of $Mo(CN)_8^{4-}$ has been confirmed, along with more accurate structural parameters, and an exhaustive exploration of the factors contributing to its dodecahedral geometry of approximate D_{2d} symmetry has been presented. The two d electrons of this anionic Mo(IV) complex occupy the d_{xy} orbital or, by the alternative symmetry definition, the $d_{x^2-y^2}$ orbital of the metal which can be used for limited π bonding with the ligands. In their discussion, Hoard, *et al.*,[4] stated that one of the two d electrons can be removed to give the paramagnetic complex $Mo^{V}(CN)_8^{3-}$ "with retention of the principal structural features"—that is, that the $Mo(CN)_8^{3-}$ anion should be dodecahedral. Electron spin resonance studies, however, have indicated that, at least in solution, the Mo(V) species exists as a square antiprism of D_{4d} symmetry.[6,7] Other physical data at this time appear to be inconclusive. Published Raman and infrared studies[8] of the $Mo(CN)_8^{4-}$ anion support the contention of D_{4d} symmetry in the solution state but are unable to eliminate the possibility of dodecahedral

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[1] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967), and references therein.

[2] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967), and references therein.

[3] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[4] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Am. Chem. Soc.*, **90**, 3177 (1968). Professor Hoard has pointed out to us that the phrase "with retention of the principal structural features" was intended to mean "only that the chemical and stereochemical integrity of the atomic grouping as a discrete eight-coordination complex" should be maintained in going from $Mo(CN)_8^{4-}$ to $Mo(CN)_8^{3-}$.

[5] J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).

[6] B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966).

[7] R. G. Hayes, *J. Chem. Phys.*, **44**, 2210 (1966).

[8] S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, **21**, 1087 (1965).