Table II. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for Compound **2a**

atom	x	y	z	U_{eq}, Å^2
Pd	0.03877 (3)	0.13463 (2)	0.18961 (3)	0.0297 (2)
C1	−0.2764 (5)	0.0545 (3)	0.0855 (5)	0.046 (3)
C2	−0.1643 (4)	0.0855 (2)	0.1256 (4)	0.032 (2)
C3	−0.0661 (4)	0.0588 (2)	0.1589 (4)	0.031 (2)
C4	−0.0461 (4)	−0.0131 (2)	0.1706 (4)	0.038 (3)
C5	0.1253 (5)	0.0665 (3)	0.4096 (5)	0.052 (3)
C6	0.1581 (4)	0.0880 (2)	0.2900 (4)	0.036 (2)
C7	0.2617 (4)	0.0849 (2)	0.2482 (5)	0.040 (3)
C8	0.3671 (5)	0.0548 (3)	0.3068 (6)	0.053 (3)
C9	0.2812 (4)	0.1160 (3)	0.1303 (5)	0.040 (3)
C10	0.3162 (4)	0.1876 (3)	0.1425 (4)	0.040 (3)
C11	0.4216 (5)	0.2071 (3)	0.1100 (6)	0.058 (4)
C12	0.4631 (6)	0.2708 (4)	0.1214 (7)	0.066 (4)
C13	0.3982 (6)	0.3170 (3)	0.1693 (6)	0.063 (4)
C14	0.2883 (5)	0.3007 (3)	0.2063 (5)	0.050 (3)
C15	0.2203 (6)	0.3479 (3)	0.2595 (6)	0.060 (4)
C16	0.1156 (6)	0.3309 (3)	0.2947 (7)	0.069 (4)
C17	0.0774 (5)	0.2678 (3)	0.2747 (6)	0.052 (3)
C18	0.2450 (4)	0.2363 (2)	0.1902 (4)	0.039 (3)
C19	−0.2583 (4)	0.1869 (3)	0.2929 (4)	0.044 (3)
C20	−0.2962 (6)	0.2339 (4)	0.3667 (5)	0.061 (4)
C21	−0.2870 (7)	0.3006 (3)	0.3382 (6)	0.071 (4)
C22	−0.2389 (6)	0.3197 (3)	0.2410 (6)	0.066 (4)
C23	−0.1940 (5)	0.2726 (3)	0.1630 (5)	0.049 (3)
C24	−0.1343 (6)	0.2928 (3)	0.0663 (6)	0.058 (4)
C25	−0.0829 (5)	0.2481 (3)	−0.0035 (5)	0.053 (3)
C26	−0.0924 (4)	0.1809 (3)	0.0219 (5)	0.042 (3)
C27	−0.1550 (4)	0.1580 (2)	0.1131 (4)	0.033 (2)
C28	−0.2059 (4)	0.2053 (2)	0.1892 (4)	0.038 (3)
C29	−0.2936 (6)	0.0980 (4)	0.4233 (6)	0.069 (4)
N	0.1353 (3)	0.2215 (2)	0.2229 (4)	0.037 (2)
O	−0.2662 (4)	0.1224 (2)	0.3116 (4)	0.056 (2)
F1	−0.3634 (3)	0.0970 (2)	0.0828 (4)	0.066 (2)
F2	−0.3066 (3)	0.0050 (2)	0.1542 (4)	0.070 (2)
F3	−0.2748 (3)	0.0307 (2)	−0.0221 (3)	0.065 (2)
F4	0.0631 (3)	−0.0301 (2)	0.1646 (4)	0.063 (2)
F5	−0.0794 (4)	−0.0375 (2)	0.2705 (3)	0.066 (2)
F6	−0.1005 (3)	−0.0489 (2)	0.0854 (3)	0.064 (2)
F7	0.1299 (5)	0.0014 (2)	0.4226 (4)	0.100 (3)
F8	0.1894 (5)	0.0902 (3)	0.4947 (3)	0.129 (4)
F9	0.0189 (4)	0.0801 (3)	0.4289 (4)	0.106 (4)
F10	0.4192 (7)	0.0186 (4)	0.2439 (7)	0.195 (7)
F11	0.3546 (5)	0.0230 (6)	0.3979 (9)	0.255 (9)
F12	0.4426 (5)	0.0971 (3)	0.3370 (8)	0.164 (6)

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compound **2a**

Pd–C3	1.998 (3)	C6–C7	1.331 (5)
Pd–C6	2.001 (3)	C7–C9	1.522 (5)
Pd–C26	2.571 (4)	C9–C10	1.526 (5)
Pd–C27	2.433 (3)	C10–C18	1.428 (5)
Pd–N	2.130 (3)	C18–N	1.392 (5)
C2–C3	1.311 (4)	C26–C27	1.392 (5)
C2–C27	1.496 (5)		
C3–Pd–C6	97.6 (2)	Pd–C6–C7	115.9 (3)
C3–Pd–C26	79.6 (2)	C6–C7–C9	119.0 (4)
C3–Pd–C27	62.5 (2)	C7–C9–C10	111.9 (4)
C6–Pd–C26	166.7 (1)	C9–C10–C18	123.1 (4)
C3–Pd–N	174.1 (1)	C28–C19–O	115.6 (4)
C6–Pd–N	87.1 (2)	C2–C27–C28	124.7 (3)
C26–Pd–N	96.6 (2)	Pd–N–C28	128.5 (2)
C27–Pd–N	112.0 (2)	C19–O–C29	120.6 (4)
C3–C2–C27	112.0 (4)		
Pd–C3–C2	104.3 (3)		

for a related compound.[5] On the other hand the insertion of Hfb into the Pd–C bond of the Pd(MXN) unit in **1a** led to a completely different bonding scheme between the new ligand and the Pd atom. As the ^{1}H NMR spectra suggested, the oxygen atom of the methoxy group is not interacting with Pd(Pd$\cdots$O > 3.5 Å). C26 and C27 are found at 2.571 (4) and 2.433 (3) Å, respectively, from the Pd atom; the angle between the C26–C27 vector and the coordination plane of Pd, defined by Pd, N, C6, and C3, is 31°. Since C26 and C27 are roughly located at the fourth coordination site of Pd, it is reasonable to assume that there must be a bonding interaction between the naphthyl ring, through the C26–C27 double bond, and the Pd atom although the Pd–C26 and Pd–C27 bond distances are rather large for a conventional carbon–carbon double-bond π bonded to such a metal.[12]

Such an interaction has never been described before between an aryl ring and a Pd(II) atom although it has been postulated by Parshall as being a likely intermediate in the CH activation reaction of an arene by this metal.[13]

It is clear from the ^{1}H NMR spectrum of compound **2c** that this η^2-naphthyl to Pd interaction causes a significative upfield shift of the corresponding aromatic protons. Compounds **2c** can reversibly bind one molecule of carbon monoxide, affording compounds **3**. The ^{1}H NMR spectrum of this compound reveals that the NMe$_2$ grouping is no longer diastereotopic and hence the CO must have displaced this unit rather than the η^2-naphthyl→Pd bond. The ortho, meta, and para protons of the part of the naphthyl group interacting with Pd are clearly found at higher frequency as compared with those of compound **1c**. This upfield shift is likely to be due to the presence of the Pd atom. The shielding effect that Pd causes upon the chemical shifts of the naphthyl protons is much less obvious in the case of compounds **2a** and **2b** because of the shielding effect that the naphthyl and the quinolyl rings exert on each other. For compound **2a**, for instance, H17 resonates at 6.04 ppm, i.e. at 2.5–3.0 ppm higher that in any related compound containing the 8-mq chelate.[4b,5,6] This can be explained by the fact that this proton is located at 2.71 Å above the plane of the naphthyl ring, and therefore it experiences the shielding of this ring. A similar trend is found for compound **2b**, the proton ortho to the nitrogen being found also at an unusually high frequency.

Registry No. 1a, 87370-34-1; **1b**, 87370-35-2; **1c**, 87370-36-3; **2a**, 106905-48-0; **2b**, 106905-49-1; **2c**, 106905-50-4; **3**, 106928-94-3; hexafluorobut-2-yne, 692-50-2.

Supplementary Material Available: An ORTEP stereoview of compound **2a** and Tables S1 and S2, listing the derived hydrogen positions and thermal parameters (3 pages); Table S3, listing calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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(12) Hartley, F. R. *The Chemistry of Platinum and Palladium*: Applied Science: London, 1973.

(13) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

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Electron Diffraction Reinvestigation of the Molecular Structure of Calcium Dihalides

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The present investigation of the molecular structure of calcium dihalides is a natural extension of our studies on first-row transition-metal dihalides (see Ref 2 and references therein). The alkaline-earth-metal dihalides themselves are also the subject of much recent structural interest. Qualitative models of bonding and structure,[3,4] empirical correlations,[4,5] semiempirical

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(1) On sabbatical leave (1984–1985) from The University of Trondheim, Trondheim, Norway.

(2) Hargittai, M.; Tremmel, J.; Hargittai, I. *Inorg. Chem.* **1986**, *25*, 3163.

(3) Coulson, C. A. *Isr. J. Chem.* **1973**, *11*, 683.

(4) Drake, M. C.; Rosenblatt, G. M. *J. Electrochem. Soc.* **1979**, *126*, 1387.

(5) Spoliti, M.; De Maria, G.; D'Alessio, L.; Maltese, M. *J. Mol. Struct.* **1980**, *67*, 159.

Table I. Experimental Conditions

	nozzle temp, K	no. of plates[a] used in analysis	data intervals, $Å^{-1}$		data steps, $Å^{-1}$
			recorded	used in analysis	
$CaCl_2$	1433				
camera range 50 cm		4	2.0–14.000	2.0–13.625	0.125
camera range 19 cm		4	9.5–35.00	9.5–30.75	0.25
$CaBr_2$	1383				
camera range 50 cm		4	2.0–14.000	2.0–14.000	0.125
camera range 19 cm		4	9.5–36.00	9.5–21.50	0.25
CaI_2	1182				
camera range 50 cm		4	2.25–14.125	2.25–13.875	0.125
camera range 19 cm		4	9.5–36.00	9.5–19.75	0.25

[a] Kodak electron image plates.

(CNDO/2) molecular orbital calculations,[6,7] and experimental evidence[8–12] are all unambiguous as to the linearity of calcium dichloride. Calcium difluoride is generally found to be bent,[3,4,7,8,13] although in an early electron diffraction study[14] no deviation from linearity was considered. The bond angle was given as 180° while the same work reported the angles for the chloride, bromide, and iodide as 180 ± 30, 180 ± 10, and 180 ± 10°, respectively. It is now generally accepted that the tendency for linear geometry strengthens as the central atom gets lighter and the halogen gets less electronegative for the second-main-group dihalide molecules. Accordingly, $CaBr_2$ and CaI_2[3,4,6,8] are accepted to be linear. There has been an electron diffraction reinvestigation of calcium diiodide by Kasparov, Ezhov, and Rambidi[15] reporting a linear geometry with large shrinkage[16] of the I···I nonbonded distance, $\delta = 0.219 \pm 0.013$ Å, from an experiment with 1300 K nozzle temperature. Their reported bond length[15] (see Table III) agrees with the result of the early work while the reinvestigation of $CaCl_2$ by Spiridonov et al.[12] resulted in a considerably smaller bond length (see Table III) as compared with that of the early study, notwithstanding the large error limits of the latter.[14] The bond lengths from the early electron diffraction study[14] are also given in Table III.

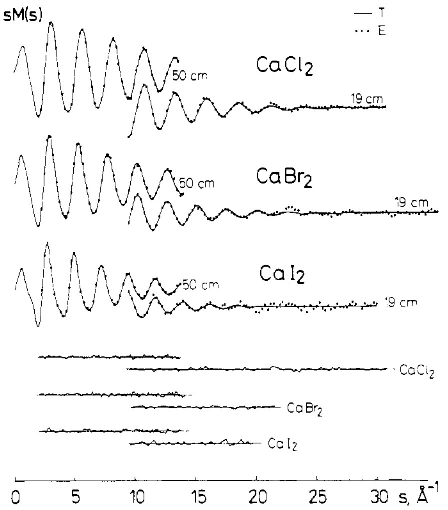

Figure 1. Experimental (E) and theoretical (T) molecular intensities and their differences for calcium dihalides.

Table II. Mean Amplitudes of Vibration Calculated with Different Approximations

	$CaCl_2$		$CaBr_2$		CaI_2	
	1[a]	2[b]	1[a]	2[b]	1[a]	2[b]
ν_1, cm^{-1}	238	291	148	177	107	126
ν_3,[c] cm^{-1}	395		330		290	
l(M–X), Å	0.130	0.119	0.137	0.126	0.138	0.129
l(X···X), Å	0.184	0.150	0.193	0.161	0.195	0.166
l(X···X),[d] Å	0.248	0.212	0.239	0.206	0.267	0.234
ν_2(ED), cm^{-1}	69		72		50	

[a] ν_1 estimated by assuming $f_{rr} = 0$.[9] [b] ν_1 estimated by Drake and Rosenblatt.[4] [c] Gas-phase experimental value.[9] [d] Calculated by a curvilinearity approximation using ν_2 values estimated from electron diffraction.

In light of the modern reinvestigation of $CaCl_2$ and CaI_2, some words of justification are warranted for the present study. Unfortunately, very little information is available on the two reinvestigations as they appeared as a conference abstract ($CaCl_2$)[12] and a brief communication (CaI_2)[15] only. The analysis of the chloride apparently involved a detailed examination and utilization of spectroscopic information, and in addition to geometrical parameters, force constants and vibrational frequencies were communicated as well, without any details, however, of the electron diffraction investigation, except the nozzle temperature (1243 K). The analysis of data did not include the asymmetry parameter (κ).[16] The electron diffraction work on CaI_2[15] involved an experiment with one camera range and was based on molecular intensities up to $s = 12$ $Å^{-1}$. With reference to a mass spectrometric study under similar conditions,[17] the presence of only monomeric species was considered. In addition to the two principal maxima on the experimental radial distribution, there was a distinct feature at about 4.3 Å, which was not commented upon in the paper.

The present electron diffraction investigation utilized the advantages of mass spectrometric control[18] and optimization of the electron diffraction experimental conditions. However small the dimer content in the vapor, it was taken into account in the structure analysis. According to our experience[19–22] even the presence of a few per cent of the dimers may have a bearing on the parameters determined for the monomer. Using two camera ranges in our experiment provided an internal check and extended the data interval for analysis. Efficient screening of our high-temperature nozzle eliminated the necessity of protecting the photographic plates from light radiation. This thereby improved

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(6) Hase, Y.; Takahata, Y. *An. Acad. Bras. Cienc.* **1982**, *54*, 501.
(7) Hase, Y.; Takahata, Y. *An. Acad. Bras. Cienc.* **1983**, *55*, 23.
(8) Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 2023.
(9) Baikov, V. I. *Opt. Spektrosk.* **1969**, *27*, 502.
(10) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1971**, *3*, 257.
(11) White, D.; Calder, G. V.; Hemple, S.; Mann, D. E. *J. Chem. Phys.* **1973**, *59*, 6645.
(12) Spiridonov, V. P.; Altman, A. B.; Gershikov, A. G.; Romanov, G. V. 2nd Conference on Determination of Molecular Structure by Microwave Spectroscopy and Electron Diffraction (5th European Microwave Spectroscopy Conference), Tübingen, West Germany, 1980.
(13) Calder, V.; Mann, D. E.; Seshadri, K. S.; Allavena, M.; White, D. *J. Chem. Phys.* **1969**, *51*, 2093.
(14) Akishin, P. A.; Spiridonov, V. P.; Sobolev, G. A. *Zh. Fiz. Khim.* **1957**, *31*, 648.
(15) Kasparov, V. V.; Ezhov, Yu. S.; Rambidi, N. G. *Zh. Strukt. Khim.* **1979**, *20*(2), 341.
(16) See, e.g.: Kuchitsu, K. In *Diffraction Studies on Non-Crystalline Substances*; Hargittai, I., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam and New York, 1981.
(17) Peterson, D. T.; Hutchison, J. F. *J. Chem. Eng. Data* **1970**, *15*, 320.
(18) Hargittai, I.; Bohátka, S.; Tremmel, J.; Berecz, I. *HSI, Hung. Sci. Instrum.* **1980**, *50*, 51.
(19) Vajda, E.; Tremmel, J.; Hargittai, I. *J. Mol. Struct.* **1978**, *44*, 101.
(20) Hargittai, M.; Hargittai, I. *J. Mol. Spectrosc.* **1984**, *108*, 155.
(21) Hargittai, M.; Hargittai, I.; Tremmel, J. *Chem. Phys. Lett.* **1981**, *83*, 207.
(22) Hargittai, M.; Dorofeeva, O. V.; Tremmel, J. *Inorg. Chem.* **1985**, *24*, 245.

Table III. Molecular Parameters of CaX_2 (X = Cl, Br, I) from Electron Diffraction[a]

	X = Cl			X = Br		X = I		
parameter	present work	ref 14	ref 12	present work	ref 14	present work	ref 14	ref 15
r_g(Ca–X), Å	2.483 (7)	2.51 (3)	2.451 (3)	2.616 (16)	2.67 (3)	2.840 (10)	2.88 (3)	2.867 (15)
l(Ca–X), Å	0.113 (3)			0.110 (4)		0.129 (4)		
κ(Ca–X), Å	11.6×10^{-5} (1.5×10^{-5})			9.6×10^{-5} (3.1×10^{-5})		9.7×10^{-5} (4.0×10^{-5})		
r_g(X···X), Å	4.746 (23)			5.082 (60)		5.458 (21)		
l(X···X), Å	0.238 (14)			0.241 (17)		0.262 (13)		
δ_g, Å[b]	0.220 (37)			0.151 (92)		0.221 (41)		
rel monomer amt, %	98.1 (8)			94.7 (15)		97.6 (7)		

[a] Estimated total errors are given in parentheses as units in the last digit. Results from earlier studies are also quoted. The errors include an estimated 0.2% experimental systematic error (see: Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *63*, 2335), and for the distances and for the shrinkage, the errors also include the influence of the dimer presence. [b] δ_g is the shrinkage, viz. $2r_g(\text{Ca–X}) - r_g(\text{X}\cdots\text{X})$.

data quality as compared with that of usual electron diffraction work at the high temperature involved in this study. In addition to these specifics, the importance of reinvestigating selected systems in different laboratories has long been recognized, and also, consistent treatment of data and vibrational corrections for series of molecules has its merits, hence the present work on the three calcium dihalides.

Experimental Section

Commercial samples were used for all three compounds. The electron diffraction patterns were taken with our modified EG-100A apparatus[23] with a high-temperature molybdenum nozzle.[24] Some of the experimental conditions are summarized in Table I. Other experimental conditions were similar to those in our studies of first-row transition-metal dihalides.[2,19–22] Listings of total electron diffraction intensities are available as supplementary material. The electron scattering factors were taken from available compilations.[25,26] The molecular intensities and radial distributions are shown in Figures 1 and 2.

Quadrupole mass spectrometric measurements under the conditions of the electron diffraction experiment revealed the presence of a few per cent of the dimers, in agreement with independent mass spectrometric evidence.[27] Accordingly, this possibility was to be considered in the analysis of the experimental data.

Structure Analysis and Results

The main features of the experimental radial distributions correspond to the structure of symmetric CaX_2 molecules. The contribution of the nonbonded interactions X···X occur at a considerably smaller value than twice the bond length. This is a consequence of shrinkage[16] and was discussed for zinc halides.[2] Asymmetries of the principal maxima and other subtle features on the experimental radial distributions pointed to the possible presence of a small amount of dimeric species in agreement with the mass spectrometric findings. Also, the asymmetry parameter, κ, in the expression of the molecular intensity was carefully examined.

Normal-coordinate analysis and calculation of mean amplitudes of vibration accompanied the electron diffraction analysis. Experimental spectroscopic information on these species are scarce. Gas-phase ν_3 values are available for all three compounds[9] and matrix-isolation ν_2 and ν_3 values for $CaCl_2$.[11] By the method of Baikov,[9] ν_1 can be estimated by assuming $f_{rr} = 0$. The relevant parameters and calculated l values are given in the "1" columns of Table II. The results of the "2" columns were obtained by using ν_1 values estimated by Drake and Rosenblatt.[4] The calculated l(X···X) values appear to be rather sensitive to the assumptions about the force field, and the agreement with the experimental l(X···X) values is not very good. Including the presence of dimeric species in the refinement somewhat improves the agreement.

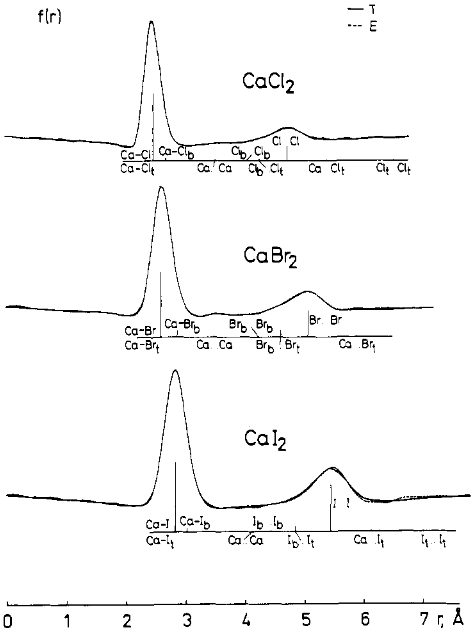
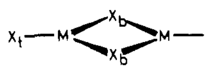


Figure 2. Experimental (E) and theoretical (T) radial distributions for the calcium dihalides.

Further improvement is brought about by the curvilinear approximation in the calculation of l(X···X) given also in Table II. As the ν_2 values are needed in these calculations, they were estimated from the electron diffraction shrinkage. The estimated value for $CaCl_2$ agrees well with the spectroscopic ν_2 value of 63 cm^{-1}.[11] The shrinkage and accordingly the estimated ν_2 value depend on whether the presence of dimeric species was considered in the refinement or not. The results that are believed to be the best representation of this analysis were obtained by including the dimeric species and emerged in an iterative process of the structure refinements and normal-coordinate analyses. They are presented in Table III.

For such small amounts of the dimers, no reliable structure determination was possible for them. However, their inclusion in the refinement is mandatory for an accurate determination of the monomer parameters. The molecular configuration for the dimer was assumed to be analogous with that determined for several of the transition-metal halide series:



The terminal M–X_t distances of the dimer were assumed to be equal with the monomer bond distance. The bridging M–X_b distance was found to be (r_g) 2.699 (44) and 2.781 (49) Å for Ca_2Cl_4 and Ca_2Br_4, respectively. The bridging bond distance of Ca_2I_4 was assumed to be 0.2 Å longer than the terminal bond distance, according to the experience with similar structures.

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(23) Hargittai, I.; Tremmel, J.; Kolonits, M. *HSI, Hung. Sci. Instrum.* **1980**, *50*, 31.

(24) Tremmel, J.; Hargittai, I. *J. Phys. E* **1985**, *18*, 148.

(25) Coherent scattering factors: Bonham, R. A.; Schäfer, L. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 176.

(26) Incoherent scattering factors: Tavard, C.; Nicolas, D.; Rouault, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1967**, *64*, 540.

(27) Emons, H.-H.; Kiessling, D.; Horlbeck, W. *Z. Anorg. Allg. Chem.* **1982**, *488*, 219.

Consideration for the asymmetry parameter (κ) was another important feature of this analysis. This parameter and its influence on the others have been examined throughout the refinements concurrently with other changes in the procedure. The first and second peaks on the experimental radial distributions display asymmetries in opposite directions. The Ca–X peaks are broader at the larger r values whereas the X···X peaks are broader at the smaller r values. Anharmonicity in the vibrations as well as the relevant contributions from the dimers are consistent sources for such asymmetries. Inclusion of κ parameters proved to be important for the M–X distance whereas this made no difference for the X···X distance. The influence of this parameter is felt increasingly at higher s values. The contributions of the X···X distances, especially with increasing atomic number of X, however, quickly diminish. On the other hand, examination of the κ parameter for the bond of $CaCl_2$ at least partially resolved the puzzle of the large discrepancy between our r(Ca–Cl) value and the result of the reinvestigation by Spiridonov et al.[12] Ignoring this parameter, we could decrease our Ca–Cl bond length by 0.015 Å, thus bringing it closer to the very low value cited.[12] The asymmetry parameter was ignored in the latter work.

The parameter κ is usually estimated as $\kappa = al^4/6$, where a is related to the Morse constant and is usually assumed to be 2 Å^{-1}. Such an assumption for Ca–Cl would give $\kappa = 5.8 \times 10^{-5}$ Å^3. The value obtained in our refinement is twice as large, and the corresponding change in the bond length is 1 standard deviation. The uncertainty in the asymmetry parameter as well as the uncertainty in the dimer content have been included as additional error source components in the estimated total errors.

In the matter of the discrepancy of our r(Ca–I) value and that of Kasparov et al., our various test calculations offered no obvious origin. However, the difference is within the combined experimental errors.

Registry No. $CaCl_2$, 10043-52-4; $CaBr_2$, 7789-41-5; CaI_2, 10102-68-8.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera ranges (50 and 19 cm) for all three compounds (6 pages). Ordering information is given on any current masthead page.

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Conformational Behavior of Co–tn Chelate Rings in Complex Compounds (tn = 1,3-Propanediamine) and Their Infrared Spectra

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In a previous study,[1] the ground-state geometry of *trans*-$[Co(CN)_2(tn)_2]^+$ in two different crystals was studied by X-ray structural analysis. It was found that in the chloride trihydrate crystal, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$, both six-membered tn–metal chelate rings of the complex *trans*-$[Co(CN)_2(tn)_2]^+$ assume the chair form, while in the chloride monohydrate crystal one is present in the chair and the other in the skew-boat form. Moreover, by analysis of the vibronic fine structure of the electronic absorption spectrum as well as by MO calculations, the distortion of *trans*-$[Co(CN)_2(tn)_2]^+$ in one of its d-electronic excited states was deduced relative to the ground state. This distortion results in a flattening of the chelate rings in the equatorial direction, as well as a contraction along the vertical axis containing the cyanide ligands. In this paper, information obtained from the infrared spectra of the above mentioned metal complexes as well as related complexes was used for a conformational analysis of the chelate rings. We performed a normal-coordinate analysis confined to a Co–tn ring and a conformational analysis of the chelate rings to assign the solid-state and solution spectra.

Experimental Section

The preparation and properties of crystals of *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$, *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$, and their N- and O-deuteriated compounds were reported previously.[1] The complex compounds *trans*-$[CoCl_2(tn)_2]Cl{\cdot}HCl{\cdot}2H_2O$,[2] *trans*-$[CoCl_2(tn)_2]Cl$,[3] *trans*-$[Co(NO_3)_2(tn)_2](NO_3)$,[4] $[Co(tn)_3]Cl_3$,[3] $[Cr(tn)_3]Cl_3{\cdot}4H_2O$,[5] and $[Cr(tn)_3][Ni(CN)_5]{\cdot}2H_2O$[6] were prepared by standard methods.

Infrared absorption spectra of the solid samples were recorded in the Nujol phase. The measurements at −15 °C were successfully performed by using a cooled sample holder in a small compartment equipped with KBr windows. The solution (D_2O) IR spectroscopy was performed with a 0.05-mm cell consisting of two KBr plates coated by thin polyethylene film with the entire sample system placed into a vigorous air stream controlled at various temperatures from 15 to 55 °C. The temperature was monitored by a thermocouple inserted between the KBr plates, which hold the Nujol mull. Small amounts of DCl were added to the D_2O solution in the case of the H compound in order to prevent deuteriation of the N hydrogens.

The ^{13}C NMR signals of solid samples were measured by the cross-polarization magic-angle spinning (C/P MAS) technique on a JEOL JNM-GX270 spectrometer equipped with a C/P MAS accessory (NM-GSH270). Samples were spun at 3–4 kHz. The pulse repetition time and the cross-polarization contact time were 5 s and 2 ms, respectively. Each spectrum required from 10 000 to 30 000 scans. Chemical shifts were measured with respect to Me_4Si via adamantane as a secondary substitution reference (29.5 ppm).

Normal-coordinate analyses were carried out at the Computer Center of Tokyo University, using the library programs BGLZ and LSMB written by Shimanouchi et al.[7]

Results and Discussion

The IR spectra of various Co(III) complexes containing equatorially oriented Co–tn chelate rings are shown in Figure 1. The spectrum in the region 800–1100 cm^{-1} of the solid *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}3H_2O$ is essentially the same as those of *trans*-$[CoCl_2(tn)_2]Cl{\cdot}HCl{\cdot}2H_2O$ and *trans*-$[Co(NO_3)_2(tn)_2]NO_3$, except for a peak that can be explained as arising from NO_3^-. These compounds were confirmed by X-ray diffraction[1,8,9] to have two chair rings arranged in a centrosymmetric C_{2h} molecular symmetry. However, the complex compound *trans*-$[Co(CN)_2(tn)_2]Cl{\cdot}H_2O$ has only one six-membered chelate ring in the chair and the other in the skew-boat form.[1] This difference in geometry is manifest by the appearance of an additional peak in this region. That is, three distinct peaks at 896, 922, and 959 cm^{-1} were observed for the monohydrated compound, while the trihydrate gives only two peaks at 890 and 933 cm^{-1}. Similarly, the complex cation *trans*-$[Co(CN)_2(tn)_2]^+$ in D_2O solution has only two IR absorption bands in this region.

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(1) Kupka, H.; Degen, J.; Urushiyama, A.; Angermund, K.; Krüger, C. *Inorg. Chem.* **1986**, *25*, 3294.
(2) Kawaguchi, H.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3453.
(3) Bailar, J. C., Jr.; Work, J. B. *J. Am. Chem. Soc.* **1946**, *68*, 232.
(4) Kawaguchi, H.; Yano, N.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1016.
(5) Schlafer, H. L.; Kling, O. *Z. Anorg. Allg. Chem.* **1959**, *302*, 1.
(6) Jurnak, F. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 2387.
(7) Shimanouchi, T. *Center News*; Computer Center of Tokyo University: Tokyo, 1968; Vol. 6, p 150.
(8) Matsumoto, K.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1903.
(9) Yasaki, E.; Oonishi, I.; Kawaguchi, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1354.

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