tertiary nitrogen attack at the planar site occupied by water. Thus, both $CuH_{-1}L$ and $CuH_{-1}L_2^-$ are very reactive with EDTA. Comparison of the log $K_H$ values, 6.7 (for $CuH_{-2}L^- + H^+ \rightleftarrows CuH_{-1}L$) and 8.7 (for $CuH_{-2}L_2^{2-} + H^+ \rightleftarrows CuH_{-1}L_2^-$), gives a thermodynamic indication of the relative ease of formation of the reactive species. Therefore, the postulated role of triglycine in the autocatalysis reaction is to facilitate the formation of a complex with only one Cu–N(peptide) bond.

Triglycine autocatalysis has also been observed[8] in the reaction of nickel–triglycine ($NiH_{-2}L^-$) with EDTA but the mechanism was not established.

Considerable experimental evidence indicates that the bonding of Cu(II) to serum albumin involves the $\alpha$-amino terminal plus one or more peptide nitrogen atoms,[10,11] in a manner similar to the bonding in copper–triglycine. Mixed complexes of copper(II) with serum albumin and several amino acids have been shown to exist in the blood in equilibrium with the copper(II)–serum albumin complex[12–16] (the major fraction of labile copper(II) in the blood). These mixed complexes have been postulated to be important intermediates in the transfer of copper from the blood to various organs and tissues.[17–20] In the present work the transfer of copper(II) from a mixed copper(II)–tripeptide complex is much faster than from the parent mono complex and this type of kinetic behavior may bear some relevance to the function of the mixed copper(II)–serum albumin–amino acid complexes in the biological transport of copper.

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# Temperature-Dependent Tetragonal Distortion in Some Thermochromic *N,N*-Diethylethylenediamine Complexes of Copper(II)

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The temperature-dependent infrared, far-infrared, and electronic spectra and magnetism of a series of thermochromic copper complexes of *N,N*-diethylethylenediamine (*asym*-$(C_2H_5)_2$en) are reported. These data, together with some existing esr data, confirm that the thermochromic behavior of these complexes arises through a temperature-dependent axial interaction between the anion and the $CuN_4$ plane, with the more square form being favored at lower temperature. In the series Cu(*asym*-$(C_2H_5)_2$en)$_2X_2$ where $X^- = ClO_4^-$, $BF_4^-$, and $NO_3^-$, the thermochromism of the tetrafluoroborate and nitrate complexes is demonstrated for the first time. In the case of the nitrate, two mutually interconvertible isomers, one square and one six-coordinate, have been isolated and identified.

The study of thermochromic materials (compounds whose color is temperature dependent) has excited interest for some time.[1] A number of such complexes were reported in a study of the products of reaction of some copper salts with various *N*-alkyl-substituted ethylenediamines.[2] Of particular interest has been the study of complexes[3–5] of *N,N*-diethylethylenediamine (*asym*-$(C_2H_5)_2$en) of molecular formula Cu(*asym*-$(C_2H_5)_2$en)$_2X_2$. The perchlorate derivative ($X^- = ClO_4^-$) is red at room temperature but turns blue above about 40°.[2,4,5] The color change is reversible. Thermochromic behavior was sought for other copper complexes of this ligand but none was found.[4] In our hands both the tetrafluoroborate salt ($X^- = BF_4^-$) and the nitrate ($X^- = NO_3^-$) were found to be reversibly thermochromic. In the latter case, two isomers, a red and a purple form, have been separately established. The electronic, vibrational, and magnetic properties of these complexes are reported here and interpreted in terms of varying tetragonal distortion.

## Experimental Section

All the complexes have been reported before.[2,6] The tetrafluoroborate complex is sufficiently thermochromic to change color (from red to purple) on contact with any warm surface, such as living skin. Since it is difficult to believe that earlier workers[4,5] could have missed this thermochromism, we assume that our preparation, which probably differs from earlier preparations (these were not adequately described so cannot be reproduced), gives rise to the product in a different crystalline phase than had previously been observed. The preparation is given below. Electronic spectra were recorded as transmittance

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TABLE I

THE EFFECT OF TEMPERATURE UPON THE VIBRATIONAL AND ELECTRONIC MAXIMA

| | | | Electronic band, nm | |
|---|---|---|---|---|
| Complex | Temp, °C | Color | Max | $\nu$(Cu–N) |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(BF_4)_2$ | +78 | Purple | 19,230 | 403 |
| | 0 | Red | 20,750 | 407 |
| | −78 | Red-orange | 21,050 | 408 |
| | −196 | Yellow-orange | 21,620 | 410 |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(ClO_4)_2$ | +78 | Purple | 19,305 | 403 |
| | +25 | Red | 20,700 | 405 |
| | −196 | Yellow-orange | 21,690 | 407 |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(NO_3)_2$ | +25 | Purple[a] | 17,605 | 395 |
| | +25 | Red | 21,460 | 414 |
| | −196 | Yellow-orange | 22,420 | 417 |

[a] Metastable isomer.

through Nujol mulls with a Cary 14 spectrophotometer. Vibrational spectra were recorded as Nujol mulls or polythene films (far infrared) with a Beckman IR 12 spectrophotometer. Variable-temperature spectra were obtained with a Beckman VLT-2 variable-temperature cell. Magnetic studies were carried out by the Faraday system using an ALPHA 4-in. pole piece variable-temperature magnetic balance which had been extensively redesigned for automatic operation.[7] The absolute error in the quoted magnetic data is probably about ±1%, but the relative errors from one temperature to another in a given experiment do not exceed ±0.25%.

**Preparation of Cu(*asym*-$(C_2H_5)_2$en$)_2(BF_4)_2$.**—Tetrafluoroboric acid (0.01 mol, 38%) was added to excess copper carbonate in the absence of solvent. When reaction was complete, absolute ethanol (50 ml) was added, and the solution was filtered from unreacted copper carbonate. This solution was then added to a stirred absolute alcoholic solution (50 ml) of the ligand *asym*-$(C_2H_5)_2$en (0.01 mol) at about 40°. A purple precipitate was formed. The solution was cooled in a refrigerator (when the solid turned red) and subsequently filtered; the product was washed with ether and dried in a vacuum desiccator. *Anal.* Calcd for $C_{12}H_{32}B_2CuF_8N_4$: C, 30.7; H, 6.9; Cu, 13.5. Found: C, 30.9; H, 7.0; Cu, 13.3.

**Preparation of the Purple Isomer of Cu(*asym*-$(C_2H_5)_2$en$)_2(NO_3)_2$.**—The preparation of this complex has been previously reported,[6] but an improved procedure is presented here. A bath of pure paraffin oil is heated to 160° and finely powdered Cu(*asym*-$(C_2H_5)_2$en$)_2(NO_3)_2$ (*red* isomer) was added while stirring vigorously. After 3 or 4 min (during which period the complex turns purple) the paraffin oil and contents are added (with care!!) to excess acetone cooled to about −50°. The solution is allowed to return to room temperature, diethyl ether added to dilute the paraffin, and the solution filtered. The product is dried under vacuum at room temperature. *Anal.* Calcd for $C_{12}H_{32}CuN_6O_6$: C, 34.3; H, 7.7; Cu, 15.1. Found: C, 33.7; H, 7.8; Cu, 14.8. Some slight decomposition occurs and perfect analytical figures were not obtainable.

## Results and Discussion

We have recently demonstrated[6] a straight-line correlation between the square of the frequency (cm$^{-1}$) of the highest energy metal–nitrogen stretching vibration and the maximum (cm$^{-1}$) of the visible absorption (d–d) band in a series of complexes Cu(N–N$)_2X_2$, where (N–N) are various diamines including *asym*-$(C_2H_5)_2$en. This correlation is dependent upon the degree of tetragonality of the complex. There is no axial interaction in the most tetragonally distorted complexes, which are four-coordinate, square, and red. At the other extreme, the axial interaction (from a halide ion for example) is quite strong, the complexes being blue and described as weakly tetragonally distorted octahedra.

For the series Cu(*asym*-$(C_2H_5)_2$en$)_2X_2$ (X = Br, Cl, $BF_4$, $ClO_4$, $NO_3$) the vibrational and electronic spectra[6] show increasing tetragonal distortion in the sequence as cited above. The halides are blue at room temperature, while the remaining three complexes are red. Not only the perchlorate but also the tetrafluoroborate complex turned blue when heated slightly above room temperature, the red color being restored on cooling. Thus, heating these two complexes apparently increases the axial interaction therein. The chloride and bromide complexes retain their blue color upon cooling, at least to −196°.

The red nitrate complex when heated to about 160° changes color, and the purple isomer produced[6] can be isolated if it is cooled rapidly to room temperature (or below). This isomer reverts to the red form very slowly at about 50° (24 hr) and rapidly above about 120° (a few minutes). Above 160° reconversion to the purple form occurs. The process red–purple–red cannot be repeated indefinitely, however, because the complex undergoes slow decomposition with loss of amine. The purple isomer cannot be obtained absolutely free from the red isomer, the amount of red isomer contaminant being dependent upon how fast the equilibrium can be frozen out by rapid cooling from 160°. At room temperature or below, the purple isomer seems to be stable indefinitely.

Table I lists electronic band maxima and the position of the highest energy copper–nitrogen stretching frequencies[6] in these complexes, as a function of temperature.

In all cases both the electronic band maximum and the metal–nitrogen stretching frequency increase with decreasing temperature and it is clear that cooling results in an increase in the tetragonality of the complex. The overall change in electronic splitting energy (from +78 to −196°) is some 2400 cm$^{-1}$ in the tetrafluoroborate and perchlorate complexes and about 4800 cm$^{-1}$ in the nitrate case. In terms of the metal–nitrogen stretching frequency the largest overall change occurs with the nitrate where the two isomers differ by 22 cm$^{-1}$ in this band energy. In the case of the perchlorate, about which so much has been written, the change in energy is only about 3 cm$^{-1}$, but is outside experimental error (±0.2 cm$^{-1}$). For the tetrafluoroborate complex it is 7 cm$^{-1}$, which is much more significant. A plot of the electronic band energy against the square of the metal–nitrogen stretching frequency for the tetrafluoroborate yields an excellent straight line (Figure 1).

**Nature of the Varying Tetragonal Distortion.**—In the case of the nitrato complexes the source of the varying distortion is clear-cut. The red complex contains ionic (uncoordinated) nitrate ions, while the purple isomer contains monodentately bound nitrato groups. These facts may be derived from consideration of the

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(7) J. Donini, B. R. Hollebone, R. A. Koehler, and A. B. P. Lever, in press.

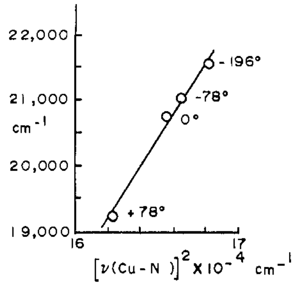

Figure 1.—A plot of the electronic band maximum against the square of the highest energy Cu–N stretching frequency as a function of temperature for Cu(*asym*-$(C_2H_5)_2$en$)_2(BF_4)_2$. Also see Figure 2 in ref 6.

combination frequencies exhibited by these complexes in the 1700–1800-cm$^{-1}$ region.[8] The red isomer exhibits a single sharp narrow band at 1750 cm$^{-1}$, while the purple isomer contains two weaker bands at 1748 and 1760 cm$^{-1}$. In these cases it is not possible to use the position and number of fundamental modes of the nitrate group as a guide to coordination behavior, because amine absorption obscures them.

There is no such clear distinction in the case of the perchlorate and tetrafluoroborate. In both red and purple forms, bands arising from the anion in a $C_{3v}$ environment can be observed. Thus the tetrafluoroborate exhibits a band at about 357 cm$^{-1}$ assigned to the $\nu_2$ (E) bending vibration, forbidden in $T_d$ symmetry but allowed in $C_{3v}$ symmetry.[9] The $\nu_3$ ($T_2$ in $T_d$) (at about 1100 cm$^{-1}$) and $\nu_4$ ($T_2$ in $T_d$) ( at about 525 cm$^{-1}$) modes were studied at various temperatures, but no splitting in either vibration was observed. The $\nu_1$ (symmetric stretching) vibration is also forbidden in $T_d$ symmetry but becomes allowed in $C_{3v}$. It is expected[9] at about 750 cm$^{-1}$. Comparison of the spectra of the tetrafluoroborate at 0° (red form) and 78° (purple form), in this region, reveals a well-defined shoulder in the latter, at 748 cm$^{-1}$, absent from the former. This is tentatively assigned as $\nu_1$.

In the case of the perchlorate, a similar situation obtains. No splitting is observed in the $\nu_3$ (near 1100 cm$^{-1}$) or $\nu_4$ (near 620 cm$^{-1}$) vibrations at room temperature or at 78°. At both temperatures a band is observed at 462 cm$^{-1}$ which is absent from the other salts and is assigned to the $\nu_2$ (E) vibration, forbidden in $T_d$, but allowed in $C_{3v}$ symmetry. The $\nu_1$ vibration is observed as a weak band at 933 cm$^{-1}$ at room temperature; at 78°, this band apparently intensifies by about 40%, while all other bands in this region broaden and decrease their apparent intensity. This provides unequivocal evidence for increased ion perturbation of the perchlorate group at the higher temperature,[10] a fact which is also inferred, but less convincingly, by the data given above for the tetrafluoroborate. The data provide evidence for a weak $C_{3v}$ perturbation of the anionic groups, which could be a site symmetry effect, but in view of the other electronic and vibrational data it seems safe to assume that it arises through coordination of one oxygen or fluorine atom to the copper, as for example is the case with the Cu(en$)_2(BF_4)_2$ complex.[9]

Hence the thermochromism in the tetrafluoroborate and perchlorate complexes arises from increased interaction of these ions with the copper ion as the temperature is raised, a fact not recognized by the earlier workers in this area[2,4] but suggested as a possible mechanism by Yokoi, *et al.*, on the basis of esr data.[5]

**Magnetic and Electron Spin Resonance Data.**—The $g$ values and susceptibilities of tetragonal copper complexes are given by the formulas[11]

$$g_{||} = 2 - \frac{8\kappa^2\lambda_0}{\Delta E_1} \tag{1}$$

$$g_{\perp} = 2 - \frac{2\kappa^2\lambda_0}{\Delta E_2} \tag{2}$$

$$\chi_{||} = \frac{N\beta^2}{kT}\left(1 - \frac{4\kappa^2\lambda_0}{\Delta E_1}\right)^2 + \frac{8\kappa^2 N\beta^2}{\Delta E_1} \tag{3}$$

$$\chi_{\perp} = \frac{N\beta^2}{kT}\left(1 - \frac{\kappa^2\lambda_0}{\Delta E_2}\right)^2 + \frac{2\kappa^2 N\beta^2}{\Delta E_1} \tag{4}$$

where $N$, $\beta$, $k$, and $T$ have their usual meaning, $\lambda_0$ is the free-ion spin–orbit coupling coefficient for copper(II) (and is negative), $\kappa$ is the orbital delocalization coefficient[12] (usually between 0.8 and unity), $\Delta E_1$ is the energy of the ${}^2B_{2g} \leftarrow {}^2B_{1g}$ transition (10$Dq$, in-plane), and $\Delta E_2$ is the energy of the ${}^2E_g \leftarrow {}^2B_{1g}$ transition. The second term in (3) and in (4) is the high-frequency or temperature-independent paramagnetic contribution (TIP).

Thus if $\kappa^2$ is assumed to be roughly temperature independent for a given molecule, then the increase in both $\Delta E_1$ and $\Delta E_2$ (these transitions cannot be resolved either at room temperature or at liquid nitrogen temperature) should result in both $g$ parameters decreasing with decreasing temperature, $g_{||}$ being the more sensitive. The data available concerning the electron spin resonance spectra of the thermochromic perchlorate confirm this supposition. Thus the $g$ values are[5] $g_{||}$ = 2.171, 2.156, and 2.117 and $g_{\perp}$ = *ca.* 2.04, 2.036, and 2.034 in polycrystalline samples at 80, 22, and −196°, respectively.

The marked sensitivity of $g_{||}$ arising from an increase in the in-plane field strength with decreasing temperature is noteworthy and consistent with the model proposed. The parallel superhyperfine interaction constant, $|A_{||}|$, increases with decreasing temperature which was considered to be consistent[5,13] with decreasing axial interaction.

The average magnetic moments of these complexes will be given by the expression

$$\mu_{\text{eff}} = \left(\frac{3k}{N\beta^2}\right)^{1/2}\left(\frac{(\chi_{||} + 2\chi_{\perp})T}{3}\right)^{1/2} \tag{5}$$

and should decrease with increasing $\Delta E_1$ (and $\Delta E_2$) as the temperature decreases. The observed magnetic moment contains the TIP term which (since it is multiplied by temperature in expression 5) introduces temperature dependency into the magnetic moment. When corrected for TIP the moment is given by

$$\mu_{\text{eff}} = 1.73\left(1 - \frac{2\kappa^2\lambda_0}{\Delta E_1}\right) \tag{6}$$

Thus, if $\kappa^2$ is constant, the corrected magnetic moment

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TABLE II

MAGNETIC DATA

| Temp, °K | $10^6\chi_M$,[a] cgsu | $\mu_{eff}$,[b] BM | $\mu_{eff}$(cor),[c] BM |
|---|---|---|---|
| Cu(*asym*-$(C_2H_5)_2$en$)_2(NO_3)_2$, Blue Isomer, LC = 226 × $10^{-6}$ cgsu, TIP[d] = 57 × $10^{-4}$ cgsu | | | |
| 116.4 | 3329 | 1.76 | 1.745 |
| 133.6 | 2903 | 1.76 | 1.74 |
| 151.1 | 2577 | 1.76 | 1.745 |
| 169.8 | 2320 | 1.775 | 1.75 |
| 188.0 | 2114 | 1.78 | 1.76 |
| 206.4 | 1936 | 1.79 | 1.76 |
| 223.1 | 1794 | 1.79 | 1.76 |
| 240.4 | 1675 | 1.79 | 1.76 |
| 259.1 | 1570 | 1.80 | 1.77 |
| 278.0 | 1470 | 1.81 | 1.77 |
| 297.0 | 1383 | 1.81 | 1.77 |
| 315.9 | 1310 | 1.82 | 1.78 |
| 334.4 | 1246 | 1.825 | 1.78 |
| 353 | 1187 | 1.83 | 1.79 |
| 364.9 | 1150 | 1.83 | 1.79 |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(NO_3)_2$, Red Isomer, LC = 226 × $10^{-6}$ cgsu, TIP[d] = 48 × $10^{-6}$ cgsu | | | |
| 99.5 | 4209 | 1.83 | 1.82 |
| 117.1 | 3579 | 1.83 | 1.82 |
| 134.7 | 3107 | 1.83 | 1.815 |
| 152.2 | 2746 | 1.83 | 1.81 |
| 170.5 | 2460 | 1.83 | 1.81 |
| 189.0 | 2224 | 1.83 | 1.81 |
| 207.7 | 2027 | 1.83 | 1.81 |
| 226.2 | 1864 | 1.84 | 1.81 |
| 245.1 | 1725 | 1.84 | 1.81 |
| 264.1 | 1603 | 1.84 | 1.81 |
| 282.9 | 1498 | 1.84 | 1.81 |
| 301.9 | 1408 | 1.84 | 1.81 |
| 321.0 | 1327 | 1.85 | 1.81 |
| 339.7 | 1253 | 1.845 | 1.81 |
| 359 | 1192 | 1.85 | 1.81 |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(BF_4)_2$, LC = 250 × $10^{-6}$ cgsu, TIP[d] = 51 × $10^{-6}$ cgsu | | | |
| 98.9 | 4109 | 1.80 | 1.79 |
| 116.3 | 3501 | 1.80 | 1.79 |
| 133.6 | 3033 | 1.80 | 1.79 |
| 150.7 | 2698 | 1.80 | 1.79 |
| 169.5 | 2409 | 1.81 | 1.79 |
| 187.4 | 2178 | 1.81 | 1.785 |
| 205.7 | 1986 | 1.81 | 1.78 |
| 224.4 | 1828 | 1.81 | 1.785 |
| 242.9 | 1692 | 1.81 | 1.785 |
| 261.1 | 1572 | 1.81 | 1.78 |
| 279.7 | 1468 | 1.81 | 1.78 |
| 298.8 | 1372 | 1.81 | 1.78 |
| 317.4 | 1293 | 1.81 | 1.775 |
| 336.1 | 1235 | 1.82 | 1.78 |
| Cu(*asym*-$(C_2H_5)_2$en$)_2(ClO_4)_2$, LC = 252 × $10^{-6}$ cgsu, TIP[d] = 49 × $10^{-6}$ cgsu | | | |
| 99.8 | 4223 | 1.84 | 1.825 |
| 117.0 | 3618 | 1.84 | 1.83 |
| 134.3 | 3139 | 1.84 | 1.82 |
| 151.6 | 2795 | 1.84 | 1.82 |
| 169.7 | 2505 | 1.84 | 1.825 |
| 187.8 | 2279 | 1.85 | 1.83 |
| 206.0 | 2083 | 1.85 | 1.83 |
| 224.4 | 1911 | 1.85 | 1.83 |
| 242.9 | 1779 | 1.86 | 1.83 |
| 261.2 | 1646 | 1.855 | 1.83 |
| 280.0 | 1545 | 1.86 | 1.83 |
| 298.95 | 1460 | 1.87 | 1.84 |
| 317.7 | 1382 | 1.87 | 1.84 |

[a] Molar susceptibility corrected for ligand diamagnetism (LC). [b] Magnetic moments inclusive of temperature independent paramagnetism (TIP). [c] Magnetic moments exclusive of TIP. [d] The TIP correction was calculated using an average value for the electronic band energy over the temperature range concerned.

is expected to decrease with decreasing temperature. The purple nitrate isomer and the perchlorate show this effect (Table II) but the other complexes have essentially temperature-independent moments. If $\kappa^2$ were to increase with decreasing temperature, then the moment may remain fortuitously constant because of the approximate constancy of the ratio $\kappa^2\lambda_0/\Delta E_1$. These results are *qualitatively* in agreement with the electron spin resonance data in that the *g* values for the perchlorate complex are moderately temperature dependent while those for the tetrafluoroborate and nitrate (red) complexes (in a nickel salt matrix) show little temperature dependence. Calculation of the magnetic moment of the perchlorate complex from the *g* values leads to agreement with experimental magnetic data to within about 0.03 BM.

If $\kappa^2$ is increasing with decreasing temperature, then it apparently has a smaller value for the more octahedral complex than for the more square complex, which would not be expected. However support for this contention comes from the observation that the moment of the purple six-coordinate nitrate isomer is smaller than its value for the red square isomer. Assuming the model indicated above for the magnetic properties, this fact can only be explained by invoking a smaller value of $\kappa^2$ for the purple six-coordinate isomer. Since a good theoretical model for the variations in $\kappa^2$ is not yet available, speculation at this time would not be profitable. Treated purely as a delocalization parameter, however, a lower value for the six-coordinate complex may simply reflect the presence of an additional number of ligating atoms over which to delocalize d electron density.

The thermochromism mechanism requires some comment. At first glance cooling the sample would be expected to favor the *less* tetragonal complex because of the contraction of the metal–ligand bond distances as higher vibrational states are depopulated. This is not the case experimentally, the more tetragonal derivative being favored. Possibly as the sample cools, the in-plane distance contracts and as a *consequence* the axial interaction weakens. At least in the case of the perchlorate complex, there is evidence of a crystal-phase change associated with the change in axial coordination.[14] Some crystals exhibit very anisotropic thermal contraction,[15] which effect, if present in these systems, could provide a mechanism for in-plane compression without corresponding axial compression. The relatively small temperature dependence of the *g* tensors of the nitrate, perchlorate, and tetrafluoroborate complexes diluted in a nickel salt matrix[5] suggests that the complexes are not thermochromic under these conditions. Thus further cyrstallographic information together with some studies of the thermal contraction of these various lattices would be useful to elucidate the thermochromic mechanism in these interesting compounds.

**Acknowledgments.**—We are indebted to both the Consiglio Nazionale delle Richerche (Rome) and the National Research Council (Ottawa) for financial support of this work.

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