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Monovalent K, Cs, Tl, and Ag Nitrosodicyanomethanides: Completely Different 3D Networks with Useful Properties of Luminescent Materials and Nonelectric Sensors for Gases[†]

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Four K, Cs, Ag(I), and Tl(I) compounds with a nitrosodicyanomethanide $ONC(CN)_2^-$ anion have been obtained and characterized using IR spectroscopy; UV−visible spectroscopy; room temperature, solid-state photoluminescence; and solutions electrical conductivity measurements. Cesium and thallium(I) complexes were obtained for the first time, and crystal structures were determined for $Cs\{ONC(CN)_2\}$, $Ag\{ONC(CN)_2\}$, and $Tl\{ONC(CN)_2\}$. These structures indicate the formation of completely different 3D polymeric networks in which the anion acts as a bridging ligand of different capacity. The cyanoxime ligand in all complexes studied is in the nitroso form and adopts a planar configuration. The structure of the cesium salt is ionic. The structure of $Ag\{ONC(CN)_2\}$ represents a 3D coordination polymer where the anion acts as a tetradentate ligand with all four bonds between Ag(I) and donor atoms (three N and one O) significantly shorter than the sum of the ionic radii for these elements. The silver(I) atom in this compound has a distorted tetrahedral surrounding. Additionally, $Ag\{ONC(CN)_2\}$ is remarkably UV- and visible-light-insensitive. However, after exposure of the solid complex to gases such as H_2, CO, NO, C_2H_2, and C_2H_4, the surface of the compound becomes *visible-light-sensitive* and changes color with significant darkening, which indicates reduction of the metal. This is reflected in a dramatic decrease of intensity of the photoluminescence of $Ag\{ONC(CN)_2\}$ in the presence of these gases, which might be utilized for nonelectric sensor applications. The $Tl\{ONC(CN)_2\}$ complex represents a transitional species between ionic (Cs) and covalent (Ag) compounds. The thallium(I) center has four shorter bonds than the sum of the ionic radii bonds (three with N and one with O atoms) and three longer electrostatic (ionic) contacts with the anion. The $6s^2$ lone pair is stereoactive, and the coordination polyhedron is best described as a distorted square pyramid. Room temperature diffusion reflectance spectra of solid $K\{ONC(CN)_2\}$, $Ag\{ONC(CN)_2\}$, and $Tl\{ONC(CN)_2\}$ demonstrated a bathochromic shift of the band's λ_{max} depending on the atomic number of the metal center, indicating a significant role of metal centers in electronic transitions in these compounds. This phenomenon was observed for the first time. The latter complex at 293 K exhibited structured metal-based red photoluminescence in the range of 690−800 nm that depends on the excitation wavelengths.

Introduction

The coordination chemistry of small cyano-group-containing anions such as dicyanamide,[1] $N(CN)_2^-$ (DCA), and tricyanomethanide,[2] $C(CN)_3^-$ (TCM), has received considerable attention in recent years due to the ability of these ligands to act as multidentate bridges in numerous 3D metal complexes. These compounds often demonstrate unusual crystal structures with fascinating lattice architectures that are useful in crystal engineering.[3] Moreover, many of these compounds have exhibited interesting magnetic properties, such as the conjugated pseudohalogenide[4] DCA and TCM anions that affirm coupling between metal centers.[5] The nitrosodicyanomethanide, $ONC(CN)_2^-$ (NDM), and nitrodicyanomethanide, $O_2NC(CN)_2^-$ (NTDM), analogues of the $C(CN)_3^-$ anion were also examined as ligands in several

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investigations of their ability to form metal complexes.[6,7] The NDM$^-$ and NTDM$^-$ anions contain a considerable mass percentage of nitrogen atoms being in both positive (formally +1 and +5) and negative (−3) oxidation states, which initiates interest for these compounds as potential high-energy materials.[8] The presence of heavy main group atoms[9] and especially heavy metal ions usually enhances the properties of these compounds. These metal ions can be oxidizers (Ag^+, $Pb^{2,4+}$, Hg^{2+})[10] or can exhibit several stable oxidation states and be involved in catalytic redox reactions (Cu^{2+}, Fe^{3+}, Co^{2+}, V^{4+}).[11] Nevertheless, the structural and coordination chemistry of NDM$^-$ and NTDM$^-$ is not well-explored, and aspects of the ligands' binding in different complexes remain largely unknown. Similarly, no information is available on other physical properties including the photoluminescence of these complexes alone or in the presence of different gaseous substances. In this paper, we report the preparation, spectroscopic and structural characterization, and solid-state emission properties of three heavy metal complexes of M$\{ONC(CN)_2\}$ composition, where M is monovalent Cs, Ag, or Tl. The effect of exposure of Ag$\{ONC(CN)_2\}$ to UV and visible light and a variety of gases is also described.

Table 1. Results of Solid-State IR Spectroscopic Studies of Several Metallo−Nitrosodicyanomethanides, $M^{n+}\{ONC(CN)_2\}_n$

compound	vibrations[a] in the IR spectra, cm^{-1}				reference
	ν^{1b}	ν^{4c}	ν^{5d}	ν^{6e}	
K$\{ONC(CN)_2\}$	2231, 2221	1326	1275	793	6, 7
^{15}N-labeled	2231, 2220	1312	1265	781	this work
NH$_4\{ONC(CN)_2\}$	2230, 2222	1325	1274	n/a	7
Cs$\{ONC(CN)_2\}$	2230*, 2216, 2205	1310	1278	786	this work
Ba$\{ONC(CN)_2\}_2$	2239, 2228	1345	1263	n/a	7
Ag$\{ONC(CN)_2\}$	2245, 2230	1334	1292	814	this work
^{15}N-labeled	2245, 2230	1316	1281	804	this work
Tl$\{ONC(CN)_2\}$	2214, 2199	1304	1279	790	this work
^{15}N-labeled	2214, 2200	1293	1267	779	this work

[a] According to ref 7. [b] Corresponds to the stretching vibration ν(C≡N) of the cyano group. [c] Corresponds to the in-plane stretching vibrations ν(C−N) and ν(N−O), as well as the bending vibration δ(C−N−O) of the nitroso group, which is also assigned as $^{as}\nu$(CNO). [d] Corresponds to the in-plane stretching vibrations ν(C=N) and the bending vibration δ(C−N−O) of the nitroso group, which is also assigned as $^{s}\nu$(CNO). [e] Corresponds to the bending in-plane NC−C−NO vibrations.

Experimental Section

Reagents. Inorganic reagents such as TlCl, AgNO$_3$, and K$_2$CO$_3$ were obtained from Aldrich, whereas CsCl was supplied by City Group Chemicals. ^{15}N-labeled NaNO$_2$ (98% enrichment) was purchased from Cambridge Laboratories. Melting points or decomposition temperatures for synthesized compounds were determined using a Mel-Temp apparatus (Thomas-Hoover). Elemental analyses of the C, H, and N content using the combustion method were performed by Atlantic Microlab (Norcross, GA).

Spectroscopic Studies. The IR spectra of all synthesized nitrosodicyanomethanide compounds were obtained at room temperature using a Nicolet FT-IR spectrophotometer equipped with OMNIC software. IR spectra of K$\{ONC(CN)_2\}$, NH$_4\{ONC(CN)_2\}$, and Cs$\{ONC(CN)_2\}$ samples were recorded using 13 mm, round KBr pellets in the range of 4000−450 cm^{-1} at 1 cm^{-1} resolution limit using 128 accumulations, whereas spectra of Tl(CCO) and Ag(CCO) were obtained from high-quality mulls prepared in mineral oil and placed between two 2 cm KBr disks. The IR spectra of these compounds are summarized in Table 1.

Solid-state diffusion reflectance spectra of fine powders of K$\{ONC(CN)_2\}$, Tl$\{ONC(CN)_2\}$, and Ag$\{ONC(CN)_2\}$ were recorded at room temperature using a Cary Bio 100 spectrophotometer equipped with a white reflectance sphere unit (Spectralon coating) using pure MgO as the reflectance standard.

Solid-state, room temperature photoluminescence spectra from fine powders of K$\{ONC(CN)_2\}$, Cs$\{ONC(CN)_2\}$, Tl$\{ONC(CN)_2\}$, and Ag$\{ONC(CN)_2\}$ were recorded on a Shimadzu RF-5301 PC spectrofluorimeter using a wooden insert for holding solid samples (Supporting Information, S1), in the range of 300−900 nm. The data sampling interval was set to 1 nm, and the slit width for both

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Table 2. Crystal and Refinement Data for Studied Compounds

parameter	Ag{ONC(CN)$_2$}	Cs{ONC(CN)$_2$}	Tl{ONC(CN)$_2$}
formula	C_3N_3OAg	C_3N_3OCs	C_3N_3OTl
mol wt, amu	201.9	226.9	298.4
color, shape	yellow block	yellow prism	orange block
crystal size, mm	0.28 × 0.25 × 0.25	0.15 × 0.18 × 0.55	0.40 × 0.33 × 0.30
temperature, K	294	296	296
density, g/cm^3	2.823	2.606	3.820
crystal system	orthorhombic	monoclinic	monoclinic
space group	P_{bca}	$P2(1)/c$	$C2/c$
unit cell, Å, °			
a	10.3063(13)	7.8163(9)	15.5346(12)
b	7.9860(10)	13.1372(15)	8.2402(5)
c	11.5458(15)	5.6498(6)	10.5347(9)
α	90	90	90
β	90	94.385(14)	129.692(6)
γ	90	90	90
volume, Å^3	950.3	578.4(11)	1037.68(14)
Z	8	4	8
abs coeff, μ mm^{-1}	4.11	6.29	31.01
total reflns	11192	9059	4380
independent reflns	1091	1762	1289
F[000]	752	408	1024
θ range, °	3.53−27.48	2.61−30.50	4.56−28.70
indexes range	$-13 < h < 13$	$-11 < h < 11$	$-20 < h < 20$
	$-10 < k < 10$	$-18 < k < 18$	$-10 < k < 11$
	$-14 < l < 14$	$-8 < l < 8$	$-13 < l < 13$
solution	direct methods	direct methods	direct methods
data/restrain/parameter	1091/0/74	1762/0/74	1289/0/73
GOF on F^2	1.089	1.107	1.139
refinement	full matrix F^2	full matrix F^2	full matrix F^2
R1 [$I > 2\sigma(I)$]	R1 = 0.0237	R1= 0.0336	R1 = 0.0276
wR2	wR2 = 0.0591	wR2 = 0.0817	wR2 = 0.0829
R indexes (all data)	R1 = 0.0245	R1 = 0.0357	R1 = 0.0290
wR2	wR2 = 0.0591	wR2 = 0.0830	wR2 = 0.0840
largest difference peak/hole (e.Å^{-3})	1.11 and −1.00	1.35 and −1.65	1.59 and −1.35

Table 3. Bond Lengths and Selected Angles for the Nitrosodicyanomethanide Anion in M{ONC(CN)$_2$} Complexes[a]

compound	bond length, Å	valence angle, °
Ag	C1−C2 = 1.424(4)	N1−C1−C3 = 123.6(3)
	C1−C3 = 1.427(4)	N1−C1−C2 = 116.1(3)
	C2−N2 = 1.142(4)	N3−C3−C1 = 178.7(4)
	C3−N3 = 1.136(4)	N2−C2−C1 = 177.8(3)
	N1−C1 = 1.331(4)	O1−N1−C1 = 116.4(2)
	O1−N1= 1.278(3)	C2−C1−C3 = 120.3(3)
Cs	C1−C2 = 1.401(5)	N1−C1−C2 = 116.9(3)
	C1−C3 = 1.407(5)	N3−C3−C1 = 177.2(4)
	C2−N2 = 1.139(5)	N2−C2−C1 = 178.4(4)
	C3−N3 = 1.139(5)	O1−N1−C1 = 117.1(4)
	N1−C1 = 1.351(5)	N1−C1−C3 = 121.6(3)
	O1−N1 = 1.250(5)	C2−C1−C3 = 121.5(3)
Tl	C1−C2 = 1.398(12)	N1−C1−C2 = 117.4(7)
	C1−C3 = 1.434(12)	N1−C1−C3 = 122.6(8)
	C2−N2 = 1.146(12)	N2−C2−C1 = 178.9(10)
	C3−N3 = 1.135(13)	N3−C3−C1 = 177.5(10)
	N1−C1 = 1.362(11)	O1−N1−C1 = 114.9(7)
	O1−N1 = 1.236(10)	C2−C1−C3 = 120.0(7)

[a] Geometry around metal centers is presented in S6, S7, and S8 in the Supporting Information.

excitation and emission was 5 nm. All spectroscopic data were processed and graphed using Origin 6.0 software.

Photophysical Measurements. To investigate the photoluminescent response of solid samples of Tl and Ag complexes in the presence of different gases, we have designed and built a special cell for these kind of measurements at ambient temperature (Supporting Information, S2). Compressed gases such as H_2, CO, acetylene C_2H_2, and ethylene C_2H_4 were obtained compressed in steel cylinders from commercial sources with purity >98%. At the same time, small quantities of pure and dry NH_3, SO_2, and NO were obtained by chemical means[33,34] from appropriate precursors (Supporting Information, S3). These gases were collected in a 1 L, round-bottom flask at ~800 Torr using standard operations with a Schlenk line and then released into a cell prevacuumed to 0.1 Torr (Supporting Information, S2) that contained solid, powdery samples of Tl{ONC(CN)$_2$} or Ag{ONC(CN)$_2$} complexes covering a 2 cm^2 area. The cell was transferred into the cuvette compartment of a Shimadzu RF-5301 PC spectrofluorimeter for measurements.

The light sensitivity and stability of synthesized Ag{ONC(CN)$_2$} were studied at 296 K using a low-pressure Hg lamp with >85% output at $\lambda_{max} = 254$ nm with the intensity of light measured by the UVX radiometer. A sample of the complex, prior to investigation, was thoroughly dried under high vacuum ($<10^{-4}$ Torr) and ground in an agate mortar. For these studies, samples of the complex were gently spread on white cardboard and covered with a black, square mask, leaving an area of 1 cm^2 for irradiation. The radiation source was positioned at a 2 cm distance from the sample (Supporting Information, S4). Digital pictures of irradiated samples were taken every 30 min using a stationary digital camera (Kodak DX7630, 6.1 Mpxl), and images were processed without the use of any filtering or enhancement using Digimax Viewer 2.0 software (Samsung).

Solution Electrical Conductivity. The electrical conductivity of 1 mM solutions of Cs{ONC(CN)$_2$}, Tl{ONC(CN)$_2$}, and Ag{ONC(CN)$_2$} in anhydrous DMSO was measured at 296 K using

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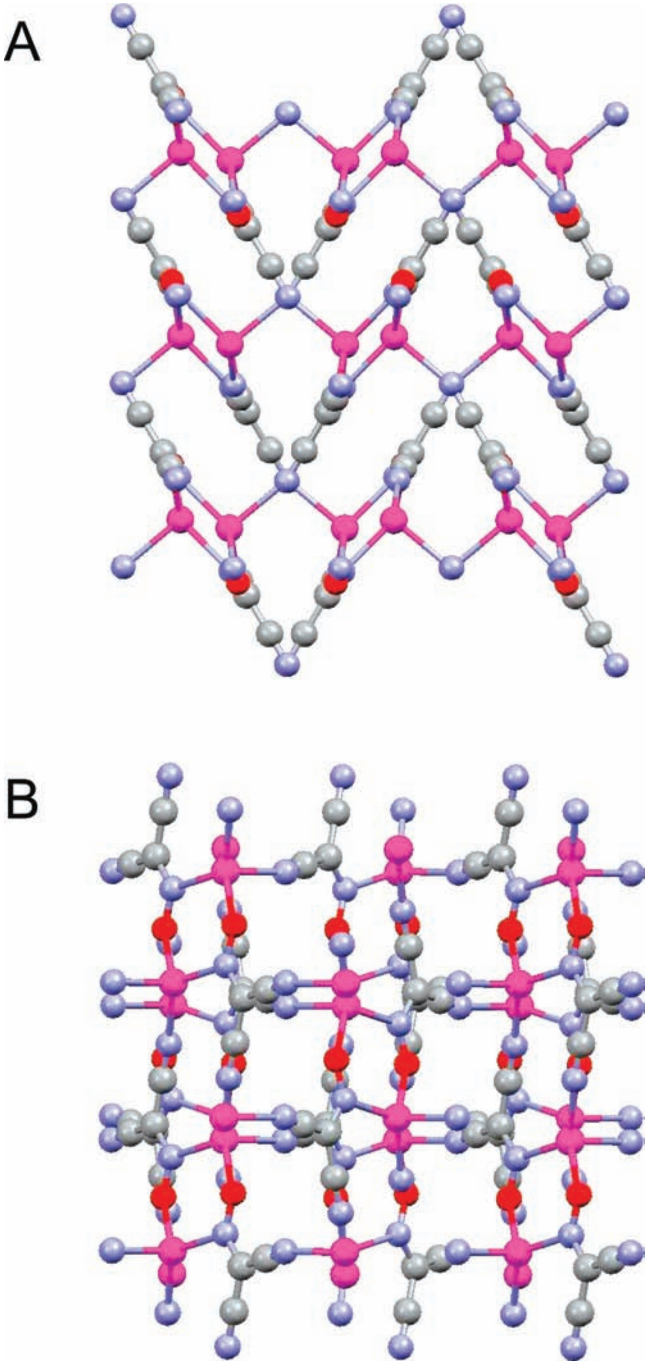

Figure 1. Fragments of the 3D polymeric structure of Ag{ONC(CN)$_2$}. Two orthogonal views of the unit cell: A, along *b*; B, along *c*. Coloring scheme: Ag, magenta; C, gray; N, blue; O, red.

a YSI conductance−resistance meter model 34. Solutions of ammonium bromide, tetrabutylammonium bromide, tetraphenylphosphonium bromide (as 1:1 electrolytes), and hydrazinium dichloride (as 1:2 electrolytes) were used for the electrode calibration.

X-ray Crystallography. Single crystals of Tl{ONC(CN)$_2$} and Cs{ONC(CN)$_2$} were obtained from aqueous solutions upon slow evaporation at 4 °C, (Supporting Information, S5). Crystals of Ag{ONC(CN)$_2$} were grown from a hot, saturated solution of the complex in water upon slow cooling in thermostat. Crystal structures were determined at room temperature from a suitable specimen mounted on a plastic fiber using thick Paraton oil. Diffraction measurements were made using a Bruker APEX2 instrument working in ω-scan mode and equipped with a SMART CCD area detector. The radiation source was a Mo tube (Kα radiation, λ = 0.71073 Å) with a highly oriented graphite monochromator. Intensities were integrated from four series of 366 exposures, each covering 0.5° in ω within 50 s of acquisition time, with the total data set being a sphere.[12] The space group determination was done with the aid of XPREP software.[14] Absorption corrections were applied on the basis of crystal face indexing obtained using actual images recorded by video camera. The following data processing was performed using the SADABS program that was included in the Bruker AXS software package.[13]The structures were solved by direct methods and refined by least-squares on weighted F^2 values for all reflections using the SHELXTL-XL program.[14] All atoms received assigned anisotropic displacement parameters and were refined without positional constraints. Crystal data for the compounds studied are presented in Table 2, whereas bond lengths and valence angles are summarized in Table 3. Figures for the crystal structures of these complexes were drawn using Mercury 4.1.2 and ORTEP 3 software[15] at 50% thermal ellipsoids probability level. The PLATON checks of crystallographic data and actual CIF files for reported structures can be found in the Supporting Information.

Synthesis. As reported in this work, K, Cs, and Tl nitrosodicyanomethanides were obtained using a heterogeneous metathesis reaction from Ag{ONC(CN)$_2$}, which is only sparingly soluble in water at room temperature. In this reaction, silver chloride is the least soluble substance:

$\mathrm{Ag\{ONC(CN)_2\}_{(s)} + MCl_{(aq)} \rightarrow AgCl_{(s)} + M\{ONC(CN)_2\}_{(aq)}}$, where M = K, Cs, Tl

The typical preparation of monovalent nitrosodicyanomethanides is given for Tl complex only.

Tl{ONC(CN)$_2$}. Ag(CCO) (0.135 g, 0.67 mM) as a fine powder was suspended in 10 mL of water by intensive stirring, at which point 0.161 g (0.67 mM) of white solid TlCl was added slowly to the suspension. The aqueous solution immediately turned a deep yellow color, and flaky white AgCl precipitate appeared. After stirring in the dark for another 20 min, the solution was filtered and washed with 2 mL of water. The clear yellow solution of Tl{ONC(CN)$_2$} was left at 4 °C for crystallization and, after 2 weeks, resulted in crystalline, dark-orange prisms suitable for X-ray analysis (Supporting Information, S5). Yield: 0.18 g (90%). Mp = 142 °C. Mp = 205−209 •C Anal. Calcd for C_3N_3OTl (Found): C, 12.07 (12.11); N, 14.08 (14.02).

Other nitrosodicyanomethanides follow.

K{ONC(CN)$_2$}. Bright yellow crystals were obtained after the

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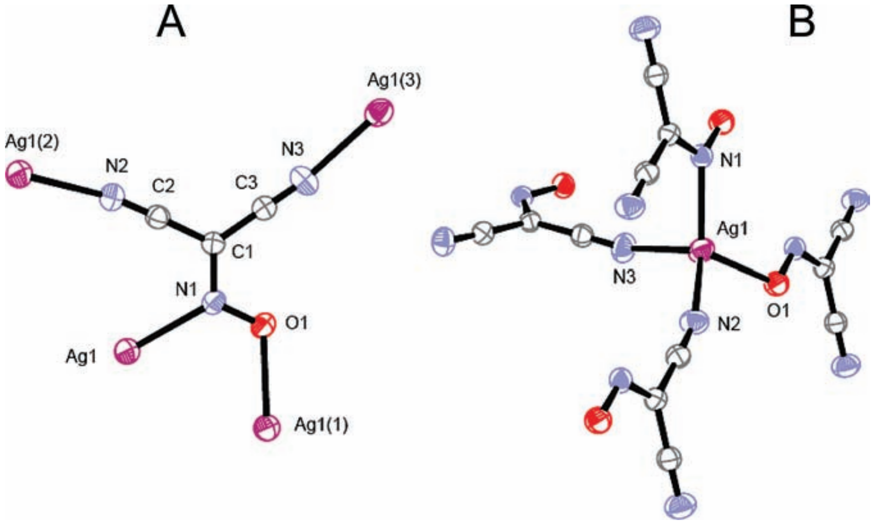

Figure 2. Numbering scheme and molecular structure of Ag{ONC(CN)$_2$}: A, one anion and closest metal ions; B, surrounding of Ag(I) center.

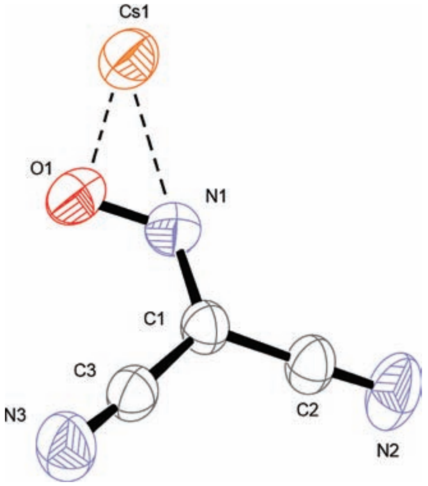

Figure 3. Asymmetric unit in the structure of Cs{ONC(CN)$_2$} with atomic numbering scheme and closest metal cation.

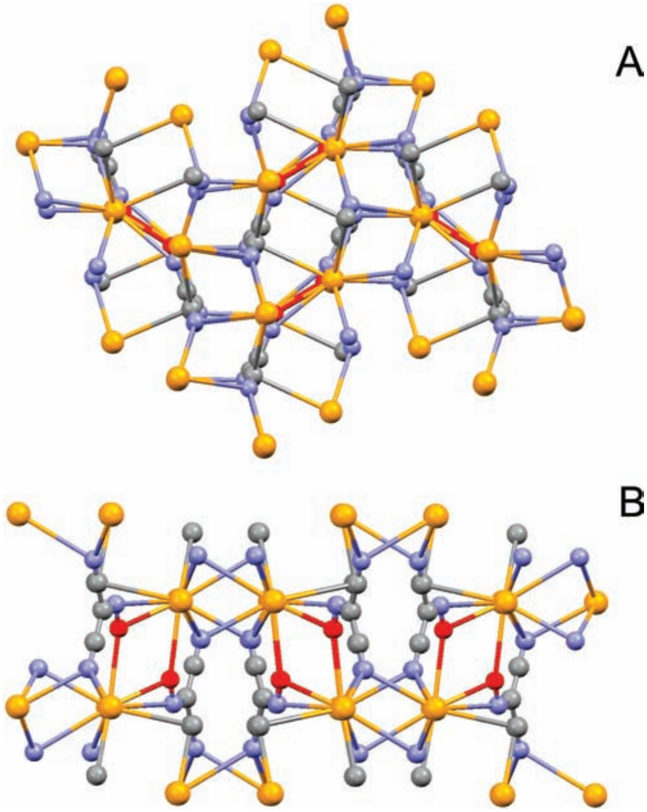

Figure 4. Fragments of the 3D ionic structure of Cs{ONC(CN)$_2$}. Two orthogonal projections of the unit cell: A, along the *a* axis; B, along the *c* axis. Coloring scheme: Cs, orange; C, gray; N, blue; O, red.

reaction of 1.00 g (5 mM) of Ag{ONC(CN)$_2$} with 0.59 g (5.0 mM) of KBr. Yield of K{ONC(CN)$_2$} = 0.65 g (98%). Mp = 205−209 °C. Anal. Calcd for C_3N_3OK (Found): C, 27.06 (27.17); N, 31.56 (31.62).

Cs{ONC(CN)$_2$}. Yellow-orange crystals were obtained after the reaction of 0.662 g (3.28 mM) of Ag{ONC(CN)$_2$}with 0.552 g (3.28 mM) of CsCl. Yield of Cs{ONC(CN)$_2$} = 0.63 g (85%). Mp = 159 °C. Anal. Calcd for C_3N_3OCs (Found): C, 15.88 (15.93); N, 18.51 (18.74).

Ag{ONC(CN)$_2$}. Bright deep-yellow microcrystalline powder was obtained (pure) after precipitation of the {ONC(CN)$_2$}$^-$ anion with $AgNO_3$ from the reaction mixture.[16] Ag{ONC(CN)$_2$} decomposes in the range of 175−210 °C. Anal. Calcd for C_3N_3OAg (Found): C, 17.84 (17.98); N, 20.81 (20.69).

The synthesis of ^{15}N (50% dilution with ^{14}N for observation of bands splitting in the IR spectra) isotopomeric compounds was carried out in a similar manner.

The obtained monovalent nitrosodicyanomethanides of K, Cs, and Tl are water soluble compounds at room temperature, whereas Ag{ONC(CN)$_2$} is sparingly soluble in boiling water. All four compounds are highly soluble in DMF, DMSO, and Py at 296 K, but not soluble in light alcohols, acetone, and chlorohydrocarbons. Both Tl{ONC(CN)$_2$} and Ag{ONC(CN)$_2$} exhibit remarkable stability to visible light (Supporting Information, S5).

Safety Note! *Although we have not encountered any problems during many years of laboratory work and handling, special care should be taken during procedures using thallium compounds because of their toxicity.*[38,39] Gloves are required at all times since solutions are easily absorbed through the skin.

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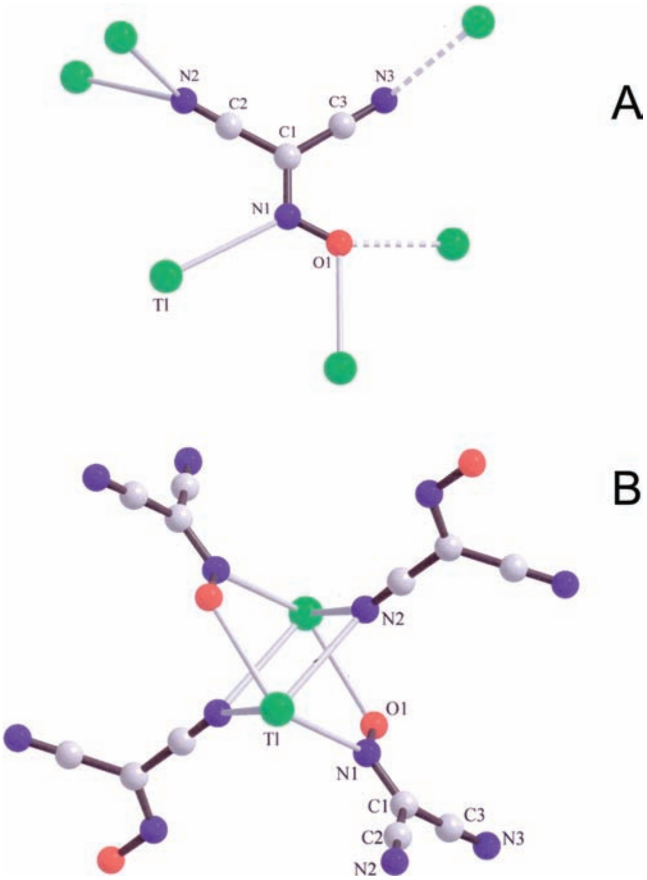


Figure 5. Numbering scheme in Tl{ONC$(CN)_2$}: A, one anion and closest Tl(I) cations; B, building block in the structure that consists of an orthogonal planar $Tl(1)_2N(2)_2$ rhomb and a planar hexagonal $Tl(1)_2N(1)_2O(1)_2$ metallocycle.

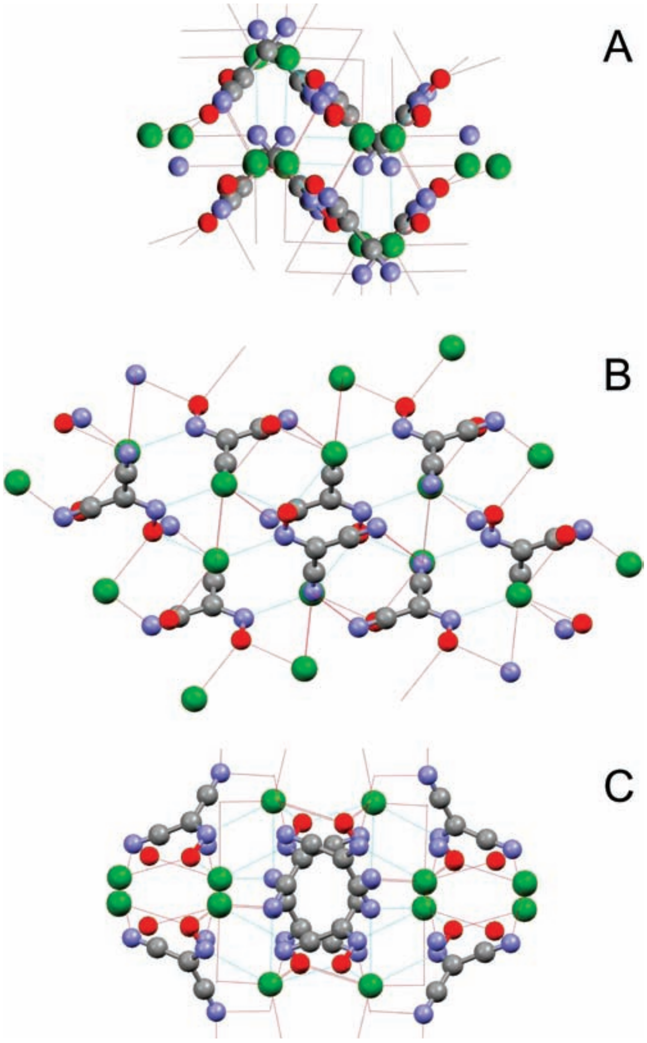


Figure 6. Fragments of the 3D network in the structure of Tl{ONC$(CN)_2$}: A, B, and C are three views of the unit cell along *a*, *b*, and *c* directions, respectively. Coloring scheme: Tl, green; C, gray; N, blue; O, red.

Results and Discussion

Structures of Synthesized M^+ Nitrosodicyanomethanides. All synthesized $ONC(CN)_2^-$-based compounds discussed in this paper represent coordination polymers of totally different structures. This can be attributed to two factors: (a) diverse ionic radii of heavy metal atoms[17] (Ag^+ for 1.26, Tl^+ for 1.47, and Cs^+ for 1.67 Å) lead to a significant increase of the cation's volume (3.79 for Ag^+, 4.84 for Tl^+, and 6.21 Å^3 for Cs^+), which affects crystal packing and (b) distinct character of binding between the anion and different cations, ranging from purely ionic for Cs{ONC$(CN)_2$}, partially covalent/ionic for Tl{ONC$(CN)_2$}, to covalent for Ag{ONC$(CN)_2$}. It is our belief that the observed structural differences in M{ONC$(CN)_2$} compounds are primarily affected by the second factor rather than the size of heavy metal cations.

Ag{ONC$(CN)_2$}. The structure of this complex was previously reported[18] in the 1970s but suffered from poor data quality and errors in the ligand bond lengths. Using modern equipment and superior crystal specimens, we were able to determine the geometry of the ligand and metal center much more accurately, although the general structural motif remained the same. Thus, silver(I) nitrosodicyanomethanide represents a 3D interwoven coordination polymer organization, which is shown in Figure 1. All donor atoms of the functional groups of $ONC(CN)_2^-$ are involved in coordination to Ag(I), therefore, bringing the denticity of the ligand to four (Figure 2). The anion is planar and adopts the nitroso form: the N1−O1 bond length is shorter (1.278(3) Å) than the C1−N1 bond length (1.331(4) Å) (Table 3). A complex polymeric structure of this compound can be dissected into planar sheets formed by four silver(I) centers and four cyanoxime anions (Supporting Information, S6). These sheets are connected via N3 atoms of identical neighboring sheets (angled at ~60°) into an interwoven 3D framework (Figure 1A). The shortest Ag(I)···Ag(I) distance is 3.677 Å. The coordination polyhedron of the Ag(I) center can be described as a distorted tetrahedron (Supporting Information, S7). All four Ag−L bond lengths are significantly shorter than the sum of Ag−O (2.58 Å)[17] and Ag−N (2.97 Å)[17] ionic radii, which indicates the covalent character of those bonds. This explains the very poor room temperature solubility of Ag{ONC$(CN)_2$} in aqueous solutions and short chain alcohols, as well as the remarkable visible-light insensitivity of the complex as observed over many years. The latter property is highly atypical of the silver(I) compounds and may have a variety of practical applications.

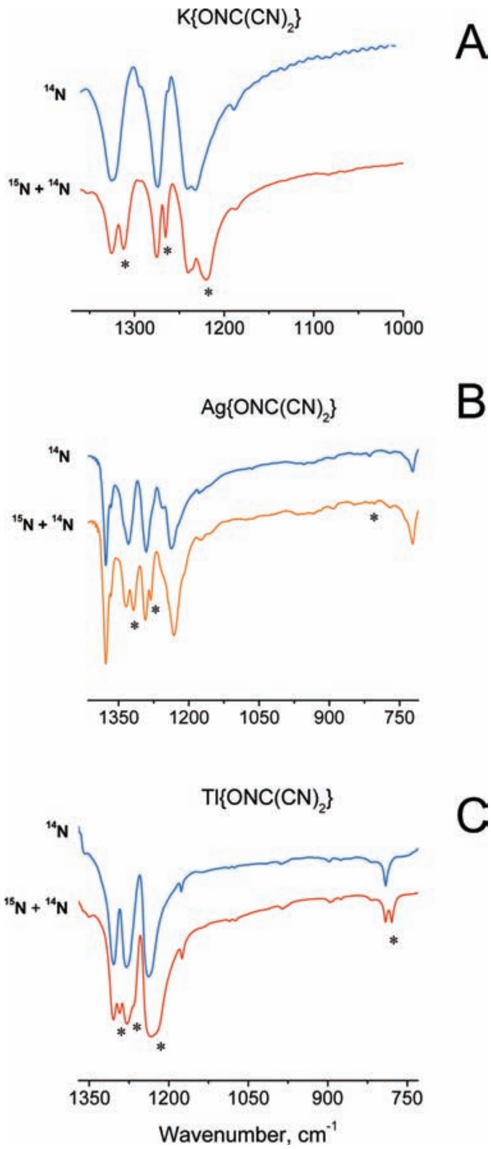


Figure 7. Overlaid fragments of the IR spectra of K{ONC(CN)$_2$} in KBr pellets (A) and Ag{ONC(CN)$_2$} and Tl{ONC(CN)$_2$} in Nujol mulls (B and C, respectively). Asterisks indicate ^{15}N isotopomer bands.

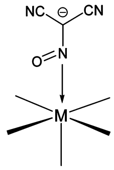
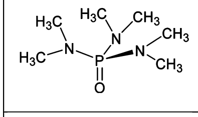
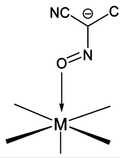
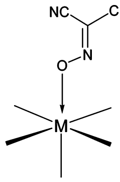
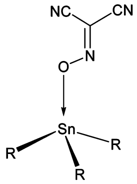
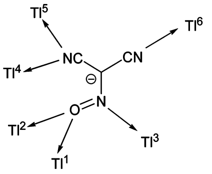
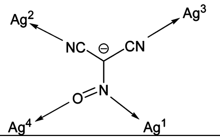
Cs{ONC(CN)$_2$}. The anion in this compound adopts planar geometry and is in the nitroso form (Table 3), judging from the N1−O1 bonds being significantly shorter than the N1−C1 bonds (Figure 3). The ONC(CN)$_2^-$ anion acts as a bridging group between several Cs centers. The Cs{ONC(CN)$_2$} is an ionic compound in which all metal−ligand distances are longer than the sum of Cs−N (3.03) and Cs−O (2.99 Å) ionic radii. For this group of compounds, especially with large metal cations, preferential binding of donor atoms to the metal center is not observed but, rather, uniform spatial distribution. There are 10 electrostatic contacts ranging from 3.053 to 3.653 Å for the Cs1 ion, which include eight nitrogen atoms and two oxygen atoms (Supporting Information, S8), with Cs1−O1 = 3.053 Å being the shortest of the ASUs. Therefore, the coordination environment of Cs1 in this compound is best described as an irregular polyhedron. The crystal packing of Cs{ONC(CN)$_2$} is rather complex and is shown in Figure 4.

Tl{ONC(CN)$_2$}. Monovalent thallium forms a completely different structure from Ag{ONC(CN)$_2$} and Cs{ONC(CN)$_2$}, although the anion acts similarly as a bridging ligand (Figure 5A and Figure S9 in the Supporting Information). First of all, there are clearly two different sets of Tl−N,O distances: four short and two long ones (Figures 6 and 7). Thus, three Tl1−nitrogen (N2,N1) bonds range from 2.93 to 3.05 Å and are shorter than the sum of the ionic radii of Tl−N = 3.18 Å,[17] indicating predominantly covalent character of these bonds. At the same time, only one thallium−oxygen bond Tl1−O1 = 2.749 Å is shorter than the sum of the ionic radii (2.79 Å) of these elements, whereas the second one is considerably longer (2.949 Å) and is responsible for bridging between building blocks during crystal packing (Figure 5B). This situation with two sets of shorter (covalent) and longer (ionic) bonds is rather typical[19] for large metal cations−“soft” acids such as Hg$^+$, Sn^{2+}, Pb^{2+}, and Tl$^+$. The ONC(CN)$_2^-$ anion in this complex is planar and in the nitroso form, which is evident from an almost purely double N=O bond equal to 1.236 Å (Table 3).

The geometry of the coordination polyhedron around Tl(I) in Tl{ONC(CN)$_2$} can be described as a distorted tetragonal pyramid and is shown in S9 in the Supporting Information. The organization of crystal packing in Tl{ONC(CN)$_2$} is complex and is shown in Figure 6 and Figure S10 in the Supporting Information. There are infinite zigzag chains of joined alternating and distorted nonplanar Tl$_2$O$_2$ rhombs and undistorted planar Tl$_2$N$_2$ rhombs that form a 3D framework with the help of a bridging anion. Because there are two different rhombs (Supporting Information, S10) in the structure, there are two Tl···Tl distances of 4.233 and 4.258 Å, respectively, but none of them can be considered as metal−metal bonds. The angle between Tl···Tl···Tl atoms is 103.8° in a zigzag chain (Supporting Information, S10).

IR Spectra. Vibrational frequencies in the IR spectra of K, Cs, Tl, and Ag nitrosodicyanomethanides are presented in Table 1, and the established binding modes of the anion are summarized in Table 4. Despite its simplicity, several different types of coordination of the ONC(CN)$_2^-$ ligand to a variety of metal centers were documented using X-ray analysis and vibrational spectroscopy with ^{15}N labels. The introduction of the label at a 50% level allowed for unambiguous assignment of stretching and bending vibrations with participation of the >C−N−O fragment in the IR spectra of each compound (Figure 7). This level of isotopic enrichment allows observation of clear splitting of the bands of isotopomers in the spectra, as opposed to just a small ~10−15 cm^{-1} shift in pure ^{15}N-enriched compounds. This shift often is not well-seen or obscured, especially if the spectra were recorded at different instrument parameters or from different samples of variable quality. Monodentate (via N or O atoms) coordination or bridging upon binding to a variety of metal ions greatly affected the position of the key $^{s}\nu$(CNO) and $^{as}\nu$(CNO) vibrations[6,7,20] (Table 4). In general, these changes correlate with the nature of the metal center in the complex (its ability to participate in π-back-bonding in the case of Fe, Ru, Ir, and Re) and reflect the distribution of electron density in the ligand (nitroso or oxime forms,

Table 4. Summarized Binding Modes of the Nitrosodicyanomethanide Ion, $ONC(CN)_2^-$ (L) in Different Complexes

Compound	Comment	Structure, binding mode	Reference
KL, NH_4L $BaL_2 \cdot H_2O$	anion is in *nitroso*-form	ionic compounds	K^+ = [24] NH_4^+, Ba^{2+}= [7b]
$ReL(CO)_5$ $IrL(CO)(PPh_3)_2$ MAm_2L_2 (M = Co, Ni, Cu; Am = dipy, phen, en) $M(py)_4L_2$	anion is in *nitroso*-form	monodentate, N-binding 	Re = [25] Ir = [7a] M^{2+} = [26] (for Co, Ni, Cu, Zn) M^{2+} = [27] (for Ni, Zn, Cu) Fe^{2+} = [28]
$ML_3(HMPA)_4$ HMPA = 	anion is in *nitroso*-form	monodentate, O-binding 	M = [29] (for Nd^{3+}) M = [30] (for Yb^{3+})
Fe(TPP)L TPP = *meso*-tetraphenylporphyrin	anion is in *oxime*-form	monodentate, O-binding 	[7a]
$R_{4-n}SnL_n$ (R = Ph, *n*-Bu; *n* = 1,2)	anion is in *oxime*-form	monodentate, O-binding 	[31]
TlL	anion is in *nitroso*-form	ampolydentate binding, bridging 	this work
AgL	anion is in *nitroso*-form	ampolydentate binding, bridging 	this work

monodentate or bridging function, etc.). Nevertheless, there are no simple or direct relationships between values of bond lengths, angles, and vibrational frequencies for the compounds studied by IR spectroscopy. As an example, the known geometric parameters of $ONC(CN)_2^-$ being monodentate in transition-metal complexes versus the IR data are summarized in S11 in the Supporting Information.

Solution Electrical Conductivity. Values of measured conductivities of millimolar solutions of compounds are presented in Table 5. The difference between three standard salts, NH_4Br, $N(C_4H_9)_4Br$, and $P(C_6H_5)_4Br$, is due to different mobility of the cations in viscous, room temperature DMSO. Clearly, ionic K^+ and Cs^+ salts of nitrosodicyanomethanide exhibit a 1:1 electrolyte ratio in solutions, closely followed by $Tl\{ONC(CN)_2\}$, whereas the $Ag\{ONC(CN)_2\}$ complex

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Table 5. Results of Measurements of Electrical Conductivity of 0.001 M Solutions of Compounds in Pure DMSO

compound	conductivity, μS	electrolyte type
DMSO	1.2 ± 0.2	
ammonium bromide, NH_4Br	43 ± 2	1:1
tetrabutylammonium bromide, $N(C_4H_9)_4Br$	24 ± 1	1:1
tetraphenylphosphonium bromide, $P(C_6H_5)_4Br$	21 ± 1	1:1
hydrazinium dichloride, $N_2H_6Cl_2$	76 ± 3	1:2
K{ONC(CN)$_2$}	40 ± 2	1:1
Cs{ONC(CN)$_2$}	36 ± 1	1:1
Tl{ONC(CN)$_2$}	34 ± 1	1:1
Ag{ONC(CN)$_2$}	28 ± 1	1:1

shows lesser dissociation. This observation is in line with results of X-ray analysis indicating covalent bonding in the Ag^+ complex, intermediate bonding between ionic and covalent for the Tl^+ complex, and the K^+ and Cs^+ salts being completely ionic.

UV−Visible Spectra. A planar conjugated yellow nitrosodicyanomethanide anion[32] forms numerous coordination compounds. The color of the $ONC(CN)_2^-$ system is due to a n → π* transition at ~390−450 nm in the nitroso chromophore. This transition is weak (ε = 20−100) and exhibits strong solvent dependence (negative solvatochromic effect).[21] The UV−visible spectra of K{ONC(CN)$_2$}, Cs{ONC(CN)$_2$}, and Tl{ONC(CN)$_2$} in water and Ag{ONC(CN)$_2$} in hot water are practically identical, which suggest the loss of structural peculiarities in aqueous solutions that are observed in the solid state. There are hydrated $ONC(CN)_2^-$ anions and K^+ and Cs^+ cations in solutions. However, solid-state reflectance spectra of synthesized and studied M{ONC(CN)$_2$} (M = K, Cs, Ag, and Tl) compounds are different and show four bands in the 320−900 nm range (Figure 8), which belong to π → π*, n → π*, and n* → π* transitions. A full line-shape analysis of solid-state, UV−visible reflectance spectra allowed for the deconvolution of four Gaussian-type bands that show very good agreement with experiment (Supporting Information, S12−S14). There

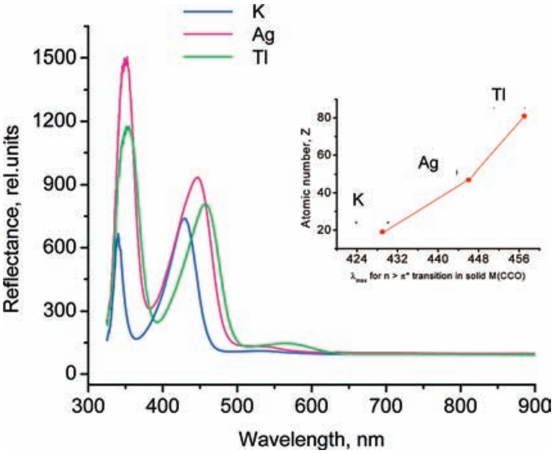

Figure 8. Diffusion reflectance spectra of M{ONC(CN)$_2$}. Inset shows the dependence of λ_{max} for the n → π* intraligand transition upon the atomic number of the metal.

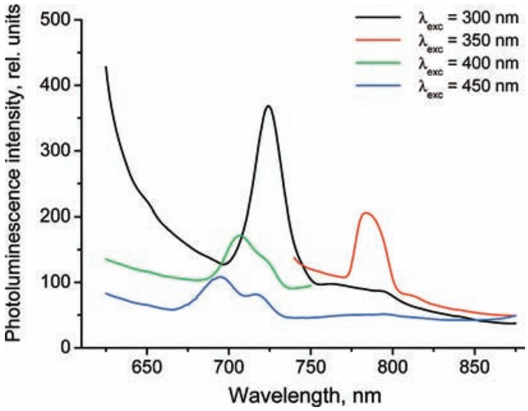

Figure 9. Unnormalized solid-state, room temperature, metal-based red photoluminescence spectra of fine powder of Tl{ONC(CN)$_2$}.

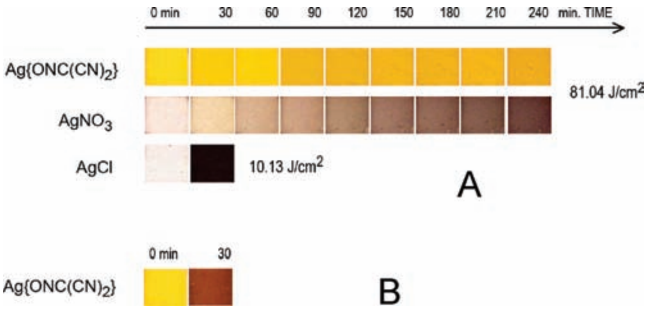

Figure 10. Results of photosensitivity studies of solid, powdery Ag{ONC)CN)$_2$} and simple inorganic AgCl and $AgNO_3$ salts toward UV radiation (λ_{max} = 254 nm) (A) and high sensitization of Ag{ONC)CN)$_2$} toward visible light after exposure to acetylene C_2H_2 (B).

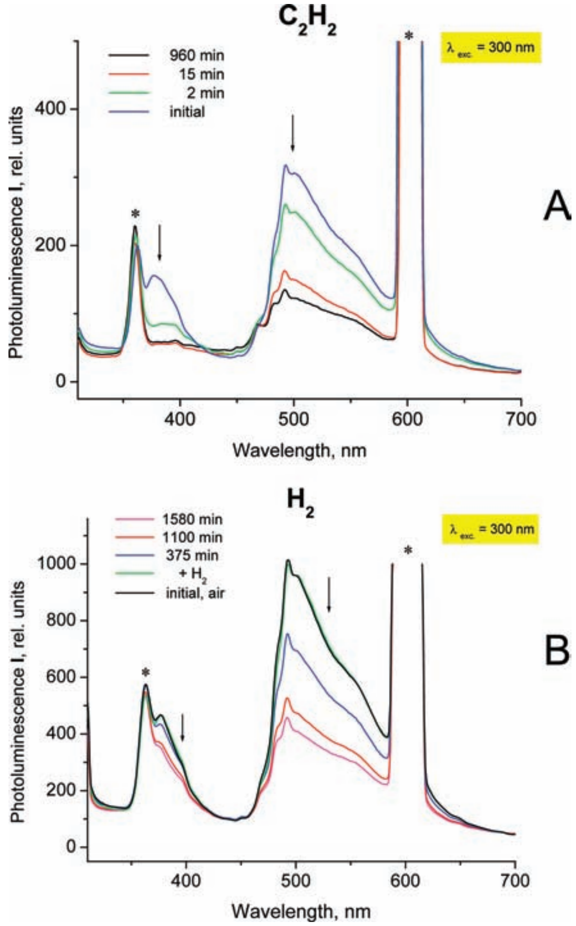

Figure 11. Changes in the photoluminescence of solid Ag{ONC(CN)$_2$} in the presence of acetylene (A) and H_2 (B). Excitation wavelength is 300 nm, and asterisks indicate instrument artifacts (multiple harmonics of the main line).

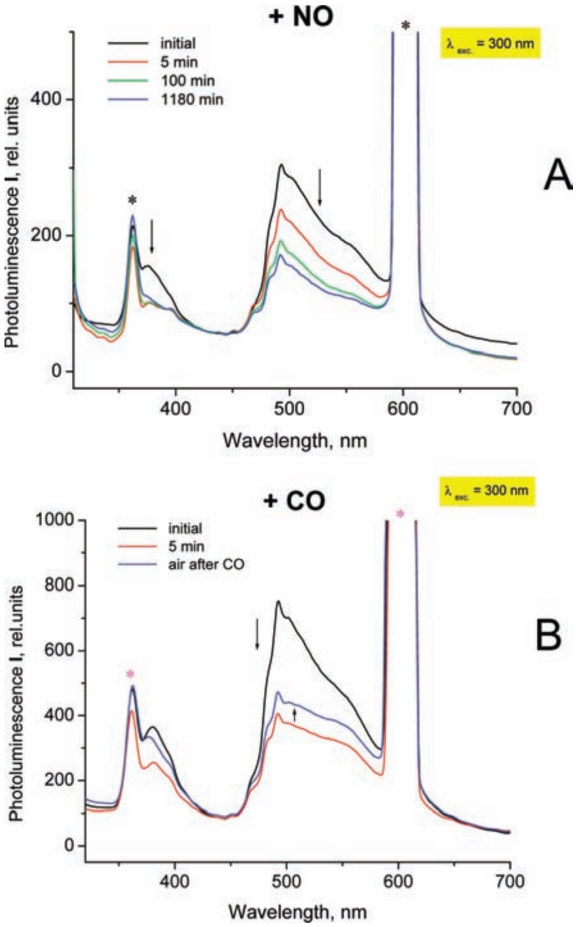

Figure 12. Changes in the photoluminescence of solid Ag{ONC(CN)$_2$} in the presence of NO (A) and CO (B). Excitation wavelength is 300 nm, and asterisks indicate instrument artifacts (multiple harmonics of the main line).

are two n → π* bands of significantly different widths in the same spectroscopic envelope (Supporting Information, S12−S14). Previously, we observed the same feature for several other cyanoxime anions,[22] but at that time, only in DMF and DMSO solutions. The most interesting feature of these spectra is that they exhibit weak broad bands for n* → π* transitions at unusually high wavelengths. Moreover, values of λ_{max} for the intraligand n → π* and π → π* transitions surprisingly demonstrate correlation with the number of electrons on the metal ion in M{ONC(CN)$_2$} compounds (Figure 8 and Figure S15 in the Supporting Information).

There is a pronounced bathochromic shift of the band positions with the increase of the atomic weight of the metal cation. This indicates definite interaction between the electrons of metal centers and the electrons of bridging anions. To the best of our knowledge, this is the first case of an established correlation between the ligand-based electronic transitions for a compound and the total number of electrons on the metal ion.

Solid-State Photoluminescence. Because studied M{ONC(CN)$_2$} compounds demonstrated interesting and completely different 3D polymeric structures, we decided to examine their solid-state emission spectra at room temperature since there was a good possibility to observe metal-based photoluminescence in these dense metal complexes. The most interesting cases turned out to be Ag{ONC(CN)$_2$} and Tl{ONC(CN)$_2$} complexes that both showed ligand-based transitions around 380 and 500 nm at room temperature. However, the thallium(I) compound also exhibited a strong metal-centered emission in the region above 650 nm (Figure 9). It appears that the shape and position of these photoluminescence signals depend on the excitation wavelength (Figure 9) where a large Stokes shift was observed between the emission and excitation maxima. This is known for monovalent Tl, which demonstrates high intensity Raman spectra in its inorganic halide complexes.[23] An assignment of a metal-to-ligand charge transfer (MLCT) state from Tl(I) to π* of the ONC(CN)$_2^-$ anion is very likely since thallium is known to form a stable Tl(III) oxidation state. In such a case, only two M → L electron transitions from the participating 6s^2 electron pair of Tl are possible due to the absence of a Tl(II) oxidation state. Also, Tl(I) is known for its long-lived excited state followed by emission of photons, which is utilized in NaI crystals, doped by Tl(I), as scincillation detectors of X-ray and γ radiation. Detailed line-shape analysis of the Tl{ONC(CN)$_2$} solid-state, room temperature emission at four studied wavelengths is presented in S16−S19 in the Supporting Information. There is only one Gaussian-type line for the λ_{exc} = 300 nm emission in the photoluminescence (PL) spectrum of Tl{ONC(CN)$_2$}, whereas two Gaussian-type lines were required to fit the experimental emission profile in the PL spectra at 350, 400, and 450 nm excitations. In all cases, these lines demonstrate significantly different line widths, which suggest different lifetimes for both excited states.

Photostablity Studies. We have mentioned a remarkable visible-light insensitivity of several silver(I) cyanoximates in the past,[35] but, in this work, we examined the stability of one particular compound, Ag{ONC(CN)$_2$}, toward short

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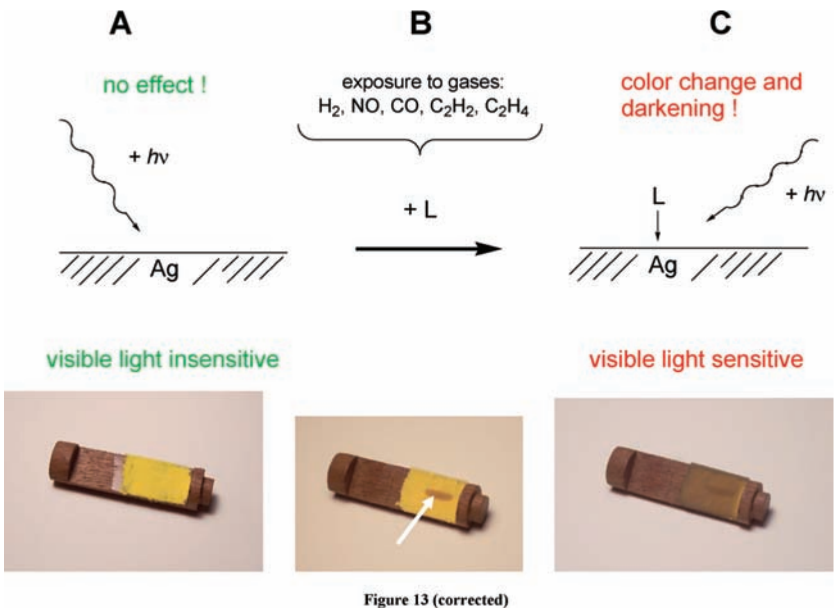

Figure 13. Change in Ag{ONC(CN)$_2$} surface color as the result of exposure to a variety of gases: A, 60 min of exposure to visible light; B, immediately after photoluminescence measurements (white arrow indicates beam area), and C, 30 min exposure to visible light. An example of interaction with nitrous oxide (NO) is shown.

wavelength UV radiation ($\lambda_{max} = 254$ nm) emitted by a low-pressure Hg lamp. We selected conventional light-sensitive, inorganic silver(I) compounds, such as $AgNO_3$ and AgCl, to compare with covalent silver(I) nitrosodicyanomethanide. Results of prolonged UV irradiation in open air are shown in Figure 10 and confirm a great stability of the Ag{ONC(CN)$_2$} complex to the treatment, during which 81 J of energy was absorbed by 1 cm^2 surface area (~25 mg) of the sample, leading to a rather small and insignificant color change as compared to control compounds. Exposure of this complex to gaseous olefins, carbon monoxide, hydrogen and nitrous oxide leads to a dramatic change in its photostability and is discussed below.

Solid-State Photoluminescence of Ag and Tl Complexes in the Presence of Gases. Samples of solid Tl{ONC(CN)$_2$} as fine powders were treated with a variety of gases to investigate their effect on the emissiveness of the complex. The thallium atom in this compound, according to X-ray analysis, is not coordinately saturated and therefore can interact with other molecules. Nevertheless, exposure of Tl{ONC(CN)$_2$} to H_2, SO_2, NH_3, NO, CO, C_2H_2, and C_2H_4 did not result in any appreciable change in its photoluminescence. A completely different story was observed when samples of dry Ag{ONC(CN)$_2$} were treated with the above pure gases. Thus, NH_3 quickly, within seconds, irreversibly quenches complex the photoluminescence, whereas SO_2 interacts with Ag{ONC(CN)$_2$} very slowly, leading to an ~8% decrease in the PL intensity, leaving the spectroscopic profile intact. Gases such as H_2, NO, CO, C_2H_2, and C_2H_4 do interact with silver(I) nitrosodicyanomethanide, which is reflected in the irreversible decrease of the photoluminescence intensity (Figures 11 and 12). The most striking feature of such interactions is that the surface of Ag{ONC(CN)$_2$} now becomes sensitized toward visible light, and the complex quickly changes color from bright yellow to dark brown. The gas was pumped out of the cell, which was filled with air prior to opening, and then the sample holder with Ag{ONC(CN)$_2$} was removed and exposed to light (Figures 10 and 13). Thus, within minutes, the compound exhibits a pronounced color change and darkening after treatment with one of the above gases (Figures 10B and 13). The effect of studied gases is only on the sample's surface since its scratching reveals the original bright yellow color. That implies sorption of the gas with chemical modification of the surface due to the formation of a complex, as we suggest in Figure 13. A chemical reaction with the surface is supported by repeated pumping of the cell for ~10 min to remove gases that might have been left inside due to physical sorption. The cell was filled with dry air prior to opening and sample exposure to visible light. Acetylene is better than ethylene sensitizer since it induces faster color change/darkening on the Ag{ONC(CN)$_2$} sample surface, which was exposed after C_2H_2 treatment to visible light. This observation is in agreement with the well-established knowledge in organometallic chemistry, that is, the much better π-accepting ability of acetylene as compared to ethylene,[36] and indirectly supports the formation of π complexes between olefins and Ag(I).

Overall, this finding can be utilized for the development of a battery-less, nonelectric sensor for the detection of H_2, CO, and gaseous olefins such as C_2H_2 and C_2H_4, which all

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are large-scale industry products. The latter two gases are flammable and frequently carried/delivered via pipe lines, so the optical detection of leaks represents an important safety issue. Ethylene, for example, is widely used in greenhouses and for ripening vegetables in containers, and is consumed in hundreds of ton quantities. Gaseous hydrogen, in turn, is thought to be one of the leading fuels for motor vehicles in the future due to its clean, "green" burning to water. Therefore, battery-less, non-electrical methods of monitoring of H_2 in close compartments becomes increasingly important. Discussed in this work, inexpensive and easy to prepare silver(I) nitrosodicyanomethanide that possesses sensoric properties might be a better alternative to apparently more costly palladium compounds recently reported by Laguna.[37] In summary, Ag{ONC(CN)$_2$} demonstrates years-long stability toward visible light, which is a very convenient property in view of the compound's color change/darkening only after exposure to gaseous H_2, NO, CO, C_2H_2, and C_2H_4.

Conclusion

We report the preparation, spectroscopic properties, and the structures of three new heavy metal complexes (Ag, Cs, and Tl(I)) of nitrosodicyanomethanide, in which the anion acts as a multidentate bridging ligand. Despite an analogous 1:1 stoichiometry, crystal structures of all three compounds are completely different and represent 3D coordination polymers of diverse complexity. The silver(I) compound forms a covalent network in which the anion is tetracoordinated via three nitrogen atoms (two of the CN groups and one of the nitroso group) and the oxygen atom of the nitroso group, with the central atom in a distorted tetrahedral surrounding. The thallium(I) compound is positioned between covalent and ionic structures; the central atom has four bonds shorter than the sum of the ionic radii of Tl−N and Tl−O and two longer electrostatic contacts. The $6s^2$ pair of Tl(I) is stereoactive and affects the structure of the coordination polyhedron, which is best described as a distorted square pyramid. The cesium complex is ionic, and the metal center has 10 contacts below 3.7 Å, of which 6 are shorter than 3.4 Å, and its structure represents an irregular polyhedron. Diffusion reflectance spectra of studied solid, monovalent nitrosodicyanomethanides in the range of 350−900 nm revealed a bathochromic shift in the band's position depending on the atomic number of the metal ion in the compound. This is the first observation of that kind of a correlation between electronic $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $n^* \rightarrow \pi^*$ transitions and the number of electrons possessed by the metal center. All three M(CCO) complexes exhibit ligand-based photoluminescence, observed as two broad bands at ~370 and ~500 nm upon excitation of solid samples in the UV region at 300 nm. However, the Tl(I) complex clearly demonstrated metal-based photoluminescence detected as a structured band in the range of 680−800 nm. Silver(I) nitrosodicyanomethanide Ag{ONC(CN)$_2$} was found to be UV-light- and visible-light-insensitive for a prolonged period of time, but it changes color and darkens while exposed to gases such as H_2, CO, NO, C_2H_2, and C_2H_4, followed by exposure to visible light. The observed photosensitization of this complex can be used in the development of nonelectric, battery-less sensors with a variety of applications.

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Supporting Information Available: Experimental setup for solid-state, room temperature photoluminescence measurements (S1); special cell for solid-state PL measurements in the presence of different gaseous substances (S2); methods of generation of small quantities of dry, pure gases (S3); experimental setup for testing of the UV-light stability of powdery, solid samples (S4); organization of 2D polymeric sheets in the structure of Ag{ONC(CN)$_2$} (S5); geometry of the coordination polyhedron in the structure of Ag{ONC(CN)$_2$} (S6); geometry of the coordination polyhedron in the structure of Cs{ONC(CN)$_2$} (S7); structure of the coordination Tl(I) polyhedron (S8); fragments of the polymeric structure of Tl{ONC(CN)$_2$} (S9); bond length and IR frequency relationships (S10); total line-shape analysis of solid-state, UV−visible reflectance spectra for K{ONC(CN)$_2$}, Ag{ONC(CN)$_2$}, and Tl{ONC(CN)$_2$} (S11−S13); plots showing bathochromic shifts of bands in the solid-state, UV−visible reflectance spectra of M{ONC(CN)$_2$} (S14); line-shape analysis of Tl{ONC(CN)$_2$} and room temperature PL at several excitation wavelengths (S15−S18); crystallographic data for the structures of Ag{ONC(CN)$_2$}, Cs{ONC(CN)$_2$}, and Tl{ONC(CN)$_2$}. This material is available free of charge via the Internet at http://pubs.acs.org.

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